Absorption studies in the light of the penetration theory

I. Long wetted-wall columns

S. Lynn, J. R. Straatemeier and H. Kramers

Laboratorium voor Physische Technologie, Technische Hogeschool, Delft

Summary—The absorption of SO_2 by water and by aqueous solutions of HCl, $NaHSO_3$ and NaCl using relatively long wetted-wall columns (12 to 22 cm) with no gas phase resistance has been investigated. The results of the investigation show (1) that in the presence of small concentrations of a surface active material (here *Teepol*, an alkyl sulphate wetting agent) the rate of absorption is very well predicted by the penetration theory, (2) that the primary function of the wetting agent is to prevent the formation of ripples in a falling film of the heights used and (3) that the hydrolysis reaction of the system SO_2-H_2O is very rapid relative to the contact times involved, so that absorption of SO_2 by water may be considered as physical absorption.

The data obtainable with this type of absorber may be used to calculate a rather reliable value of the product $C^{\bullet} \sqrt{D}$ in the case of physical absorption. If this product is known, the absorber may be used to study reaction rates in chemical absorption.

Résumé—On a étudié l'absorption de SO_2 pure dans l'eau et dans des solutions aqueuses de HCl, $NaHSO_3$ et NaCl avec une colonne à parois mouillées, de 12 à 22 cm. de longueur. Les expériences démontrent (1) qu'en présence de faibles concentrations d'un détergent (*Teepol*) la vitesse d'absorption peut être prédite avec la theorie simple de diffusion non-stationnaire, (2) que la fonction primaire du détergent est de supprimer les ondulations à la surface du liquide, et (3) que la réaction d'hydrolyse du système SO_2-H_2O est très rapide auprès les temps de contact utilisés (entre 0,1 et 1 seconde).

Pour l'absorption physique, des expériences dans un absorbeur comme utilisé ici peuvent fournir une valeur assez sûre du produit $C^{\bullet} \sqrt{D}$. Au cas où cette valeur soit connue, l'absorbeur peut être utilisé pour l'étude de vitesses de réaction chez l'absorption avec réaction chimique.

1. Introduction

The penetration theory of absorption in the absence of gas-phase resistance, first proposed by Higbie [1] in 1935, has long been recognized as being intuitively more reasonable than the stagnant liquid film concept which is used so widely in practical design work. While many investigators [2, 3, 4] have used the penetration theory to correlate their data, however, attempts to verify the theory quantitatively have not been highly successful. Reasons for this have been the appearance of ripples on the liquid films, unknown end- and begin-effects, inexact methods of analysis and various other complications. As a result, the precision of the data has generally been low. The present investigation was undertaken in an attempt to verify the penetration theory quantitatively for a very simple flow situation.

As applied to the case of a falling liquid film, the basic assumptions of the penetration theory are as follows : Gas is absorbed by an element of area on the surface of the film as if the surface element were saturated during the first instant of exposure, and as if the liquid behind the element

were an infinitely deep stagnant layer during the time, t_c, in which the element moves from the top of the column to the bottom. Thus, the velocity of that part of the film through which the solute diffuses during t_c is considered to be constant, and the diffusion in the direction of flow is assumed to be negligible. These assumptions are expressed in the following familiar differential equation and its boundary conditions

$$D \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t}, \quad \begin{array}{l} C = C_0 \text{ for } x > 0, t = 0 \\ C = C^* \quad ,, \ x = 0, t \geqslant 0 \\ C = C_0 \quad ,, \ x = 0, t < 0 \end{array} \quad (1)$$

where D = diffusivity of the solute in the liquid, cm^2/sec,

C = concentration of diffusing solute, g/cm^3,

C^* = concentration of solute at saturation, g/cm^3,

C_0 = initial concentration of solute in bulk of liquid, g/cm^3,

x = coordinate in the direction of diffusion cm,

t = time, sec.

The rate of absorption, Φ_m (g/sec), of an element of area at time t is then

$$\frac{d\Phi_m}{dA} = (C^* - C_0) \sqrt{\frac{D}{\pi t}}$$

and the average rate of absorptoin per unit area, Φ''_m (g/cm^{2}sec), for the whole column can be shown to be

$$\Phi_m'' = \frac{1}{t_c} \int_0^{t_c} (C^* - C_0) \sqrt{\frac{D}{\pi t}} \, dt$$
$$= 2 (C^* - C_0) \sqrt{\frac{D}{\pi t_c}}, \quad (2)$$

where t_c is the total contact time of an element of area.

For the case of a film formed on the outside of a cylindrical tube, the area A, of the film surface is

$$A = 2\pi (r + \delta) h_e, \quad (3)$$

where h_e = the effective height of the column,

r = the radius of the tube,

δ = the thickness of the film.

The thickness of the film is determined by the density and viscosity of the liquid and by the flow rate. For laminar flow it is given by

$$\delta = \sqrt[3]{\frac{3 \nu \Gamma_e}{g}}. \quad (4)$$

where ν = kinematic viscosity, cm^2/sec,

Γ_e = volumetric rate of flow per cm, cm^3/cm sec.

g = acceleration due to gravity. 981 cm/sec^2.

The velocity of the surface of the film is similarly determined by the nature of the liquid and the flow conditions and for laminar flow is

$$v_i = \frac{3}{2} \frac{\Gamma_e}{\delta}. \quad (5)$$

The flow has been found to be essentially laminar [5] for values of Re below 1200 when Re is defined as

$$Re = 4 \frac{\Gamma_e}{\nu}.$$

The time during which an element of area on the surface of the film is in contact with the gas as it moves from the top of the column to the bottom is

$$t_e = \frac{h_e}{v_i} = \frac{2}{3} \frac{\delta h_e}{\Gamma_e}. \quad (6)$$

Thus, the average rate of absorption per unit area for the column becomes

$$\Phi_m^* = \frac{\Phi_m}{2\pi (r + \delta) h_e} = 2 (C^* - C_0) \sqrt{\frac{3 D \Gamma_e}{2\pi \delta h_e}}$$
$$= 2 (C^* - C_0) \left(\frac{3D}{2\pi}\right)^{1/2} \left(\frac{g}{3\nu}\right)^{1/6} \Gamma_e^{1/3} h_e^{-1/2}. \quad (7)$$

DANCKWERTS [6] has provided a means of estimating the conditions under which the assumptions of an infinitely thick layer moving at a constant velocity are no longer approximately valid. From a graphical solution of the differential equation for diffusion in a finite film moving with a parabolic velocity profile he found that the effect of the wall and the velocity gradient did not change the rate of absorption by more than 5% so long as the value of the dimensionless

group $\dfrac{h\,D\,\nu^*}{g\,\delta^4}$ is less than 0·1. For the smallest value of Γ_i used in this set of experiments the corresponding value of h should thus be less than 200 cm, a condition which is met with quite a wide margin of safety in these experiments.

2. DESCRIPTION OF EQUIPMENT

A schematic diagram of the equipment is shown in Fig. 1. Water was throttled through a valve from a pressure of two atmospheres through a rotameter and into the absorber. The purpose of having the water supplied under pressure was to prevent small changes of pressure in the absorber from affecting the liquid flow rate.
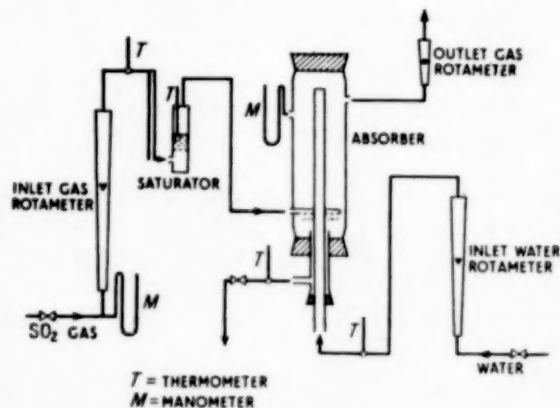

T = THERMOMETER
M = MANOMETER

FIG. 1. Sketch of absorption apparatus.

The water flowed into the absorber through a vertical tube made of stainless steel with an outer diameter of 15 mm. The surface of the tube was roughened slightly by sand blasting to facilitate wetting by water, and the tube wall was slightly rounded at the top. The water entered at the bottom of the tube and flowed out over the top and down the sides as a falling film. The liquid level in the receiver at the bottom of the film was kept constant, the height of the column

---

* The substitution of eqs. (4) and (5) in this group yields $\dfrac{h}{4v_i}\Big/\dfrac{\delta^2}{2D}$ or, in other words, the ratio

$\dfrac{\text{residence time}}{\text{diffusion time constant}}$ must be less than 0·4.

being varied by moving the tube rather than by changing the liquid level.

SO_2 from a cylinder flowed first through a large rotameter and was then saturated with water before being admitted into the absorber. The incoming flow rate of the SO_2 was always greater than the rate at which the gas was being absorbed, and the excess passed out through a second, much smaller rotameter in the outlet line. The flow through the smaller rotameter was about 5% of the incoming flow. By thus maintaining a small steady stream of gas through the absorber, the accumulation of insoluble gaseous impurites at the liquid interface was prevented. The temperatures of the incoming gas stream, of the water in the saturator, and of the incoming and outgoing liquid streams, and the pressure in the absorber and before the gas rotameter were measured for each experimental point. Small adjustments of the data were then applied to obtain the rate of absorption at 20°C and a partial pressure of SO_2 of 750 mm Hg. These adjustments will be discussed in more detail in another section.

Ordinary distilled water was used. Preliminary experiments indicated that the amount of air dissolved in the water as the result of the pressurization of the feed vessel had no measurable effect on the gas absorption. The SO_2 used was 99·9% pure, the impurities being H_2O and SO_3. The solutions of sodium bisulphite were made from the purest commercially available supply of that salt. The normality of the solutions was determined by acidimetric titration. The sodium chloride solutions were made up by weight.

3. TREATMENT OF DATA

For ease of comparison, the data obtained were all adjusted to a constant value of the surface temperature of the water film and a constant value of the partial pressure of SO_2 within the absorber. The average temperature of the surface of the film was assumed to be 1°C above the average of the inlet and outlet temperatures (see Section 5). The rate of absorption at the average temperature of the experiment (16°, 20°, or 24°C) was then calculated by assuming the thermal coefficient of absorption to be $-1\cdot6\%$/°C, a value

which is based on the penetration theory (see Section 4, A) and which was verified by experiment. Thus, the rate of absorption observed, for example, at an average surface temperature of 20·5° was increased by 0·8% to obtain the value for 20°. The adjustments made in this manner rarely exceeded 2% and were usually less than 1%.

The partial pressure of the SO_2 in the absorption vessel was computed by subtracting the vapour pressure of water at the temperature of the water in the saturator from the absolute pressure in the vessel.

The concentration of SO_2 at the surface of the film, and hence the rate of absorption of SO_2 in the liquid, was assumed to be directly proportional to the partial pressure of SO_2 in the vessel. Thus, the rate of absorption observed, for example, at a partial pressure of SO_2 of 755 mm Hg was decreased by 0·67% to obtain the rate at 750 mm Hg. These adjustments too, were usually less than 1%.

4. RESULTS AND CONCLUSIONS*

A. *Agreement of the data with the penetration theory*

If, for a certain gas-liquid system, one has dependable values for all of the parameters of equation (7), one may test the penetration theory quantitatively for that system. Lacking one of the parameters, one may use the absorption data of the system as a means of determining its value by assuming the theory to hold. In the present case, a combination of these two procedures was employed.

The terms in equation (7) subject to the most uncertainty for the SO_2-water system are, of course, C^* and D. Values of the former found in the literature disagree by about 7%, those found for the latter disagree by nearly 50%. Since it was thus necessary to make an arbitrary choice of the parameters used, we chose the following procedure. Absorption data were taken with the flow rate, column height, and temperature as independent variables. A value of C^* was selected from the literature, and a value of D was then

---

* No numerical results have been tabulated in this paper but they can be requested from the authors.

calculated from the data for one height and temperature. Since the temperature coefficients of D and C^* are fairly well known, it was then possible to check the penetration theory by the variation of the absorption with temperature and column height.

The data on the solubility and dissociation of SO_2 in water were taken entirely from the work of JOHNSTONE and LEPPLA [7]. Their results are presented in terms of an ionization constant and a Henry's law constant which are given as functions of the temperature. Their values for these constants and the total solubility differ from those given by other authors. They are used here, however, because they are consistent with each other and can easily be used in calculating the effect of temperature on the rate of absorption.

In Fig. 2 are shown the data for the rate of absorption of SO_2 by a solution of 0·0050 wt.% surface active material (*Teepol*) in water for columns of different heights. The effective height, h_e, of the column was obtained by measuring the actual height, h, and adjusting for the entry effect in the following manner : The area of the liquid surface on the top of the tube is more than πr^2
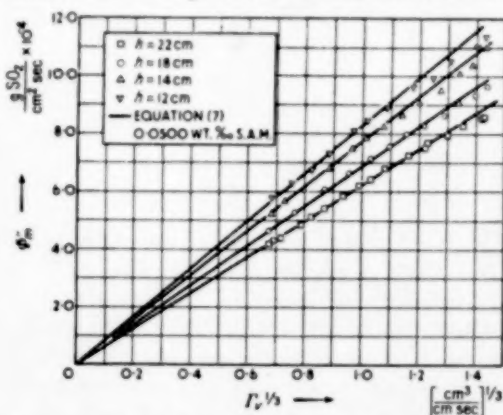

FIG. 2. Rates of absorption for different heights of column.

and less than $2\pi r^2$, i.e., the surface area is between that of a circle and a hemisphere. It was taken arbitrarily to be $3/2\pi r^2$, which can be expressed in terms of an increase in the height, Δh, of $\frac{1}{4}r$. The liquid in the receptor, being relatively stagnant, was assumed to absorb SO_2 at a negligible rate.

The solid lines in Fig. 2 were calculated from equation (7). For C^* at 20°C a value of 0·0995 g SO_2/cm^3 (data of JOHNSTONE and LEPPLA [7]) was taken. It was found that a value of D at 20°C of $1·46 \times 10^{-5}$ cm²/sec. fits all the experimental data. This value is in the same range as those found by other investigators. KOLTHOFF and MILLER [8] reported $1·78 \times 10^{-5}$, PEACEMAN [2] found $1·55 \times 10^{-5}$, WHITNEY and VIVIAN [9], as will be mentioned later, based their calculations on a value of $1·66 \times 10^{-5}$ and GROOTHUIS and KRAMERS [10] found $1·4 \times 10^{-5}$ cm²/sec.* The above values have been interpolated, where necessary, to 20°C by assuming $D\mu/T$ to be a constant.

The scatter of the data in Fig. 2 is remarkably low for absorption work. The straight portions of curves drawn through the experimental points in Fig. 2 would lie within ½% of the respective theoretical lines. Since a deviation of the experimental points from the theoretical curves of only 2% would be significant, it is felt that the agreement of the two over a range of column heights of slightly less than a factor two provides a sufficiently rigorous test of the theory for the purposes of this paper.

Furthermore, as can be seen in Fig. 3, equation (7) equally well predicts the change in absorption with temperatures, caused by variations in C^*, D and μ.

The departure of the curves of Figs. 2 and 3 from linearity at the higher flow rates is believed to be due primarily to the increasingly greater effect of the entrance conditions. This effect is relatively more important for the shorter columns, as would be expected. The deviation of the points from the theoretical line becomes important at increasingly lower flow rates as the height of the column is decreased. The minimum height of the type of column used in these experiments was thus determined by these entry effects.

B. The effect of the presence of Teepol

Many observers studying absorption and desorption with wetted-wall columns have reported that at certain flow rates and column heights the rates of absorption measured are much higher than those predicted by the penetration theory. This effect has generally been attributed to ripples on the film surface. These ripples are always observable when the rate of absorption is abnormally high, and are not found when the rate of absorption is normal. EMMERT and PIGFORD [3], as well as others, found that the addition of a small amount of an alkyl sulphonate (" Petrowet ") eliminated the ripples and decreased the absorption. They also found, however, that as the concentration of this wetting agent was increased the rate of absorption went through a minimum, showing an optimum concentration for the elimination of ripples. ZERNOVSKAYA and BELOPOLSKII [11] found that the presence of a minimum depended on the type of surface active material used.

The effect of the ripples on the gas absorption depends a great deal on the height of the column being used. At low flow rates the ripples appear quite close to the top of the column, and the amplitude of the ripples is relatively high. As the flow rate is increased, the ripples begin to form at points increasingly farther from the entrance, and the amplitude of the ripples decreases. A column of any height could presumably be ripple-free at sufficiently high flow rates if it were not for the onset of turbulence in the film.

The addition of a surface active material to the water lowers the point on the column at
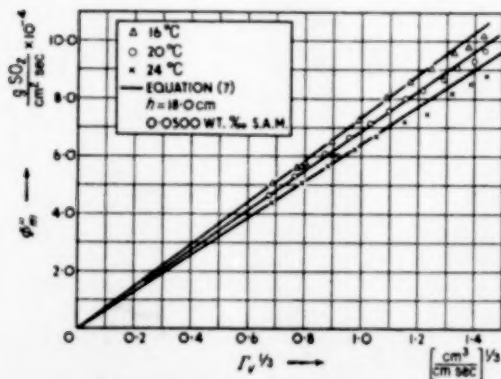

FIG. 3. Rates of absorption at different temperatures.

---

* The authors' value also agrees very well with the semi-empirical correlation of SCHEIBEL (*Ind. Eng. Chem.* 1954 46 2007) and WILKE (*Chem. Eng. Prog.* 1949 45 218).

which the ripples begin to form. The effect of the wetting agent used, an alkyl sulphate marketed under the trade name of *Teepol*, on the absorption is shown in Fig. 4. The hump in the absorption curve of pure water is gradually ironed out as the *Teepol* concentration is increased. At the highest flow rates, where even the pure water does not exhibit ripples, it is seen that the absorption by the water is nearly the same as that of the *Teepol* solutions.
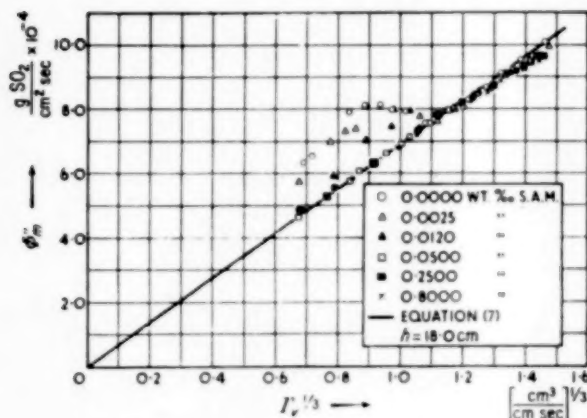

FIG. 4. Effect of surface active material on the rate of absorption of SO_2 in water.

C. *The hydrolysis of SO_2 in aqueous solution*

According to ROTH [12] in a saturated solution of SO_2 in water the SO_2 is present in three forms : unhydrated, hydrated and ionized. JOHNSTONE and LEPPLA [7] reported that the concentration of unionized SO_2 in aqueous solution varied with the partial pressure of SO_2 in accordance with Henry's law, and gave values for the Henry's law constant which were based on their measurements of the solubility and the values of the ionization constant which they had chosen. As the result of measurements made with a packed column, WHITNEY and VIVIAN [9] suggested that the rate of the ionization reaction might be slow in relation to the contact times involved in their column. This assumption can be checked by comparing the rate of absorption in water with the rate of absorption in a solution which suppressed the ionization reaction. One should find

a distinctly lower rate of absorption by an acid, for instance, if the ionization reaction were fast, and very little difference in the rates of absorption if the ionization reaction were slow.

A saturated solution of SO_2 at normal pressure and temperature is about 1·6 M in SO_2 and about 0·18 N in hydrogen ion, i.e., about 11% ionized. Because the saturated solution is so concentrated, it is necessary to use acid or bisulphite solutions of high ionic strength in order to suppress the ionization by a measurable amount. Therefore, absorption measurements were carried out with 3 N HCl, and 1 N and 0·2 N $NaHSO_3$. In addition solutions of 1 N and 0·2 N NaCl were used in order to provide, for comparison, an idea of the effect of ionic strength alone. It is assumed that NaCl forms no complexes with SO_2. All the solutions contained 0·0050 wt.% *Teepol*.

The results of these tests are shown in Fig. 5. The lines on the figure represent equation (7) for water and the sulphite solutions. To make the calculations, the concentration of unionized SO_2 in the sulphite solutions was assumed to be the same, when expressed in grams per thousand grams of water, as it is in pure water. The partial specific volume of SO_2 was assumed to be the same in the sulphite solutions as in water, and the term $D\mu$ was assumed to be a constant. A summation
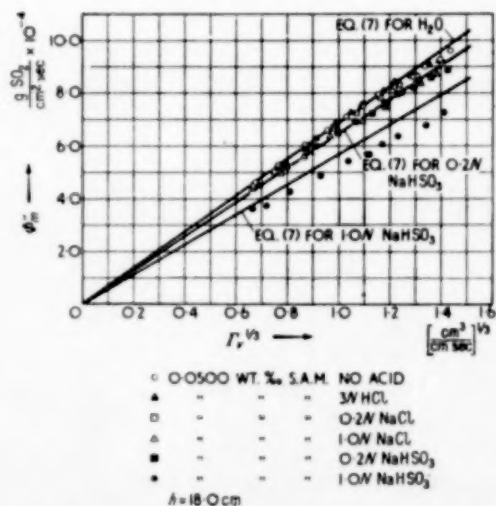

FIG. 5. Comparison of the rates of absorption of SO_2 in water and in solutions of $NaHSO_3$, NaCl and HCl.

Table 1. *Pertinent physical and chemical properties of solutions used.*

Solution	$\gamma\pm$	$C^*_{H^+}$ (calc.)	$C^*_{HSO_3^-}$ (calc.)	$C^*_{H_2SO_3}$ (calc.)	μ, 20°C g/cm sec	D, 20°C 10^{-5} cm²/sec	ρ, 20°C g/cm³	$\left[2(C^* - C_0)\left(\dfrac{3D}{2\pi}\right)^{1/2}\left(\dfrac{g}{3\nu}\right)^{1/6}\right] \times 10^3$ (calc.)	(exp.)
H₂O	0·82	0·0108	0·0108	0·0887	0·0100	1·46	0·998	2·97	2·95
0·2 N NaCl	0·74	—	—	—	0·0102	1·43	1·004	—	2·77
1·0 N NaCl	0·66	—	—	—	0·0109	1·34	1·038	—	3·00
2·84 N HCl	—	—	—	—	—	—	1·045	—	—
0·196 N NaHSO₃	0·74	0·0075	—	0·0885	0·0104	1·40	1·011	2·78	2·80
1·087 N NaHSO₃	0·66	0·0025	—	0·0865	0·0117	1·25	1·075	2·43	2·26

$$\log_{10} H = \frac{1368\cdot43}{T} - 7\cdot37566$$

$$\log_{10} K = \frac{843\cdot33}{T} - 4\cdot71507$$

$$H = \frac{\text{moles } SO_2}{1000 \text{ g } H_2O} \Big/ p_{SO_2} \text{ (mm Hg)}$$

$$K = \frac{[H^+][HSO_3^-]}{[H_2SO_3]}, \qquad [\ ] = \frac{\text{moles}}{1000 \text{ g } H_2O}$$

of the pertinent physical and chemical properties of the solutions, measured and calculated, is given in Table 1.

The rate of absorption by the 1 N bisulphite solution is retarded even more than is predicted on the basis of reduced ionization and a smaller diffusion coefficient. This is not surprising, since one would expect a certain salting-out effect by the NaHSO₃ on the unionized SO₂, and the predicted change in the diffusivity coefficient is little more than a guess. The magnitude of these two effects may be estimated by comparison to the absorption by NaCl solutions. As is seen in Fig. 5 0·2 N NaCl absorbs at nearly as great a rate as water, while 1 N NaCl absorbs at a rate which is about 5% smaller.

The rate of absorption by 3 N HCl was found to be the same as that of water. This is surprising, since one would expect both a lower solubility of SO₂ (due to retarded ionization) and a lower diffusivity (because of a higher viscosity) in the acid. Rough solubility measurements indicated, however, that the equilibrium concentration of SO₂ in 3 N HCl is about 15% greater than that of water. It thus appears that the agreement in the rates of absorption is simply a coincidence.

The evidence given above, in favour of a fast hydrolysis reaction, is persuasive but not conclusive. The data could all be interpreted as being in accord with the concept of a slow hydrolysis reaction if it were assumed that the diffusion coefficients in the bisulphite solutions were reduced much more than the change in viscosity would indicate. Such an assumption, while drastic, can not be dismissed, *a priori*, as an impossibility.

Additional data, however, obtained by a completely separate method, appear to settle the question beyond doubt. An apparatus was constructed which permitted the rapid mixing of a stream of water and a stream of liquid SO₂, and the subsequent measurement of the electrical conductivity of the solution obtained. In the steady-state flow obtaining, complete mixing was produced in a time interval of 0·1 second, and the conductivity was measured for times between 0·1 and 1·0 second. Using the conductivity data of MORGAN and MAASS [11], it was found that

even at temperatures as low as 4°C, the hydrolysis reaction was at least 90% complete within the shortest time interval which could be measured.

Whitney and Vivian made their assumption of a slow hydrolysis reaction in order to correlate their absorption data with that of other investigators. Their data can be correlated just as easily by assuming a lower value of the diffusion coefficient than they used. As mentioned above, the variations in the values of D found in the literature are sufficiently wide to give one a great deal of freedom in making a choice of a value to use.

In the light of the data and arguments presented above, it appears that the rate of the hydrolysis reaction of SO_2 in water is fast relative to the diffusion process. Thus, one may assume that the surface of a water film is instantaneously saturated at the equilibrium concentration upon exposure to SO_2. It follows that the absorption of SO_2 in water may be treated as physical absorption.

5. Discussion of Errors

The random error, as can be seen from the plots of the experimental data, is quite small, about $\pm 1\%$. It arises from uncertainties in reading the rotameters and thermometers and in determining the height of the column.

The systematic errors include both the uncertainties in the calibration of the equipment and also the uncertainties in the assumptions involved in the estimation of the surface on the top of the column, of the changes in solubility due to temperature and pressure (i.e. of the corrections made to present the data for a standard temperature and pressure), and of the surface temperature of the film.

The estimation of the equivalent height of the column involves a two-fold assumption; first an estimation of the surface of the liquid on the top of the column and second an estimation of the velocity at the surface. Both are necessary in order to estimate the time of contact of an element of surface area. However, the value of Δh amounts to only 5-10% of h, so that a relatively large error in the estimation of Δh will not greatly alter the relationship of the gas absorption to height, since this varies with $h_e^{\frac{1}{2}}$.

The estimation of the actual temperature of the interface is subject to the most uncertainty of all the assumptions involved. If the film actually behaved as a semi-infinite stagnant layer, the surface temperature would remain constant. However, the thermal diffusivity of water is of the order of a hundred times greater than the diffusivity of SO_2 in water, so that, whereas the assumption of constant velocity and infinite depth is justifiable for the diffusion of material in the films considered, it is not at all justifiable for the diffusion of thermal energy.

One can calculate the temperature rise of the surface of the film due to the absorption of SO_2 (Danckwerts [14]). If one takes the heat of solution of SO_2 in a saturated solution to be 6·7 Kcal/mol (Roth [12]) this rise is found to be about 1·0°C. For want of a better assumption the average temperature of the surface of the film was taken as the average of the inlet and outlet water temperature plus 1°C.

It is estimated that the total uncertainty due to systematic errors is $\pm 5\%$, the greatest part being due to the temperature of the surface of the film.

6. Limits of Applicability

The conditions studied here were for effective column heights between 12·5 and 22·5 cm and for Reynolds' numbers between 123 and 1150. This corresponds to contact times between 0·13 and 0·98 seconds. Lower flow rates were not studied because of the difficulty in keeping the tube completely wet by the solution. Measurements with shorter tube lengths were not included because of the increasing relative importance not only of the entrance effect but also of an exit effect.

This exit effect is evidenced by the appearance of a band of ripples about a centimetre above the level of the liquid in the receptor. Preliminary qualitative experiments indicate that the surface of the falling film below this band of ripples is nearly stagnant, and that the height of the band of ripples varies inversely wih the velocity of the falling film. A similar phenomenon has been reported by Matsuyama [15], who studied absorption by short liquid jets. This effect will be discussed in Part II of this paper.

ACKNOWLEDGMENT

NOTATION

A = area of film surface, cm^2

C = concentration of diffusing solute, g/cm^3

C_0 = initial concentration of solute in bulk of liquid, g/cm^3

C^* = concentration of solute in saturated solution, g/cm^3

D = diffusivity of solute in liquid, cm^2/sec

g = acceleration due to gravity, $981\ cm/sec^2$

h = height of column, cm

Δh = increment in height to account for entry effect, cm

h_e = effective height of column, $h + \Delta h$, cm

r = radius of tube, cm

Re = Reynolds' number of film

T = absolute temperature, °K

t = time, sec

t_c = contact time of an element of area in the column, sec

v_i = velocity of the surface of the liquid film, cm/sec

x = coordinate in the direction of diffusion, cm

Γ_v = volumetric rate of flow per centimetre, cm^3/cm sec

$\gamma_\pm$ = mean activity coefficient of positive and negative ions

δ = thickness of liquid film on wall of column, cm

μ = dynamic viscosity, g/sec cm

ν = kinematic viscosity, cm^2/sec

Φ_m = rate of absorption, g/sec

Φ_m'' = rate of absorption per unit area, g/cm^2 sec

REFERENCES

[1] HIGBIE, R.; *Trans. Amer. Inst. Chem. Eng.* 1935 31 325.

[2] PEACEMAN, D. W.; Sc.D. Thesis, *Chem. Eng. M.I.T.* 1951.

[3] EMMERT, R. E. and PIGFORD, R. L.; *Chem. Eng. Prog.* 1954 50 87.

[4] BRÖTZ, W.; *Chem. Ing. Tech.* 1954 26 470.

[5] DUKLER, A. E. and BERGELIN, O. P.; *Chem. Eng. Prog.* 1952 48 557.

[6] DANCKWERTS, P. V.; *Ind. Eng. Chem.* 1951 43 1462.

[7] JOHNSTONE, H. F. and LEPPLA, P. W.; *J. Amer. Chem. Soc.* 1934 56 2233.

[8] KOLTHOFF, I. M. and MILLER, C. S.; *J. Amer. Chem. Soc.* 1941 63 2818.

[9] WHITNEY, R. P. and VIVIAN, J. E.; *Chem. Eng. Prog.* 1949 45 323.

[10] GROOTHUIS, H. and KRAMERS, H.; *Chem. Eng. Sci.* 1955 4 17.

[11] ZERNOVSKAYA, A. N. and BELOPOLSKII, A. P.; *Zhur. Fiz. Khim. (U.S.S.R.)* 1950 24 43.

[12] ROTH, A.; *Z. Phys. Chem.* 1935 A173 313.

[13] MORGAN, O. M. and MAASS, O.; *Can. J. Research* 1931 5 162.

[14] DANCKWERTS, P. V.; *Appl. Sci. Res.* 1953 3A 385.

[15] MATSUYAMA, T.; *Mem. Fac. Eng. Kyoto University* 1953 15 142.

Absorption studies in the light of the penetration theory

II.   Absorption by short wetted-wall columns

S. Lynn, J. R. Straatemeier and H. Kramers

Laboratorium voor Physische Technologie, Technische Hogeschool, Delft

Summary— The rate of absorption of SO_2 by water in short wetted-wall columns (heights of 1 to 5 cm) with no gas phase resistance has been investigated.   When the liquid film emerges through a slit of appropriate width, the entrance effect is negligible and need not be considered in applying the penetration theory to the rate of absorption.   However, there is a considerable end-effect which is evidenced by a thickening of the film, accompanied by an apparent stagnation of the surface, on the lower one centimetre of the column.   The rate of absorption by this part of the film is relatively low.   This phenomenon complicates the analysis of data obtained with short wetted-wall columns, or other equipment with films flowing over small distances.

Résumé—On a mesuré la vitesse d'absorption de SO_2 pure dans l'eau dans un absorbeur à paroi moillée avec un hauteur de 1 à 5 cm.   Si l'eau est alimenté par une fis-ure d'une largeur appropriée, la correction d'entrée, qu'il faudrait introduire dans la theorie de la " pénétration " pour calculer l'absorption, parait être negligeable.   D'autre part, il se produit une région avec une grande resistance pour l'absorption à la partie inférieure de la surface de l'eau.   En certains cas cette partie peut avoir une hauteur de 2 cm.   L'apparition de cet effet est visible par une faible augmentation de l'épaisseur de la couche, qui est accompagné par une corrugation de la surface.   Par l'effet signalé ici l'analyse de la résistance de la phase liquide à l'absorption se complique, surtout quand il s'agit d'un appareil, où des couches de liquide parcourent des trajets courts.

1.   Introduction

In the first article of this series [1], the absorption of SO_2 by water using relatively long wetted-wall columns was discussed.   Columns with effective heights between 12·5 and 22·5 cm were studied using pure SO_2 (thus no gas-phase resistance), and were found to obey the penetration theory quantitatively.   It was shown that the film behaved as a semi-infinite layer with the surface suddenly saturated with SO_2, and that the rate of absorption Φ_m (g/sec), for the column was expressed by the following formula :

$$\Phi_m = 2\,(C^* - C_0)\,A\,\sqrt{\frac{D}{\pi\,t_e}}, \qquad (1)$$

where C^* = concentration of solute at the surface (g/cm³)

C_0 = initial concentration of solute in bulk of liquid (g/cm³)

A = area of film surface (cm²)

t_e = time during which an element of area on the surface is exposed to gas (sec)

In the previous study the water flowed down the outside of a vertical tube which was open at the top.   This produced an entry effect whose magnitude could not be estimated with great accuracy.   For the study of short columns the top was covered with an accurately centred cap, which formed an entry-section for the film of water.   The distance required for the surface of the film to accelerate to 90% of the equilibrium velocity was estimated by the use of a scaled-up model and found to be about 12 times the film thickness.   Thus, the entry-effect is negligible and need not be considered in applying the penetration theory to the rate of absorption.

In the course of the experiments with both the long and the short columns, it was found that at a certain height above the surface of the stagnant

liquid in the receiver, into which the film of water flowed, the thickness of the film increased from the normal to a slightly greater value. This was accompanied by the appearance of a narrow, horizontal band of ripples at the top of the thickened portion of the film. The height of this end-effect was found to vary in an inverse manner with the velocity of the film, from 2 cm for the lowest flow rate used to 0·1 cm for the highest. An effect similar to this has been observed by MATSUYAMA [2], who studied absorption by a short jet of liquid. However, the effect apparently escaped the attention of PEACEMAN [3] and EMMERT and PIGFORD [4], who have also worked with short columns.

Qualitative experiments indicate that the surface of the film below the ripples is nearly stagnant. A light powder (lycopodium seed) blown onto the surface of the film circles lazily instead of being swept immediately into the liquid receiver. A coloured liquid introduced in the surface layers of the film accumulates to form a dark-coloured band below the ripples [5].

If the surface of the film below the ripples were actually stagnant, the rate at which that area absorbed gas would be very much lower than that of the much fresher liquid above the ripples. One may consider two extremes : (1) when the area of this end-effect is a comparatively small fraction of the total film area and (2) when the end-effect has reached the top of the column so that the surface of the entire film is apparently stagnant.

In the first situation, the rate of absorption of the area below the ripples may be neglected relative to that of the fresher surface. The column may thus be considered to be shorter by the height of the end-effect, h_r. Using the relationship between the contact time, t_c, and the liquid flow rate, acceleration of gravity, and the physical properties of the fluid given in [1], equation (1) then becomes

$$\Phi_m = 4\,(C^* - C_0)(r + \delta)\left(\frac{\pi D}{2}\right)^{\frac{1}{2}}\left(\frac{9g}{\nu}\right)^{\frac{1}{6}} \Gamma_v^{\frac{1}{6}}\, h_e^{\frac{1}{2}}, \quad (2)$$

where h_e = effective height of column, $(h - h_r)$, cm.

In the second situation it is assumed that the liquid issuing from the entry-section, remains in full parabolic flow, with zero velocity at the surface. It is thus analogous to the case of heat transfer to a liquid in laminar flow between parallel plates when the liquid enters a section where one plate has a different, constant temperature and the other is perfectly insulated. So far as is known, the literature contains no solution of the differential equation obtaining in this case.

However, for sufficiently low values of the term $hD/\delta\Gamma_v$, the solution may be approximated from the solution for the symmetrical case when the liquid enters a section where both plates have the same different, constant temperature. The rate of heat transfer in the former case will be just half that in the latter case, in the first approximation (in reality it will be somewhat greater than half). The solution for the latter case has been calculated by PRINS, MULDER and SCHENK [6]. Using the notation of this paper, their results may be expressed in the following formula :

$$\frac{\Phi_m}{2\pi r\,(C^* - C_0)\,\Gamma_v} = f\left(\frac{hD}{\Gamma_v\,\delta}\right), \quad (3)$$

where δ, for flow due to gravity between vertical parallel plates, is

$$\delta = \sqrt[3]{\frac{12\,\nu\,\Gamma_v}{g}}.$$

The value of the term $\dfrac{\Phi_m}{2\pi r\,(C^* - C_0)\,\Gamma_v}$ as a function of $\dfrac{hD}{\delta\,\Gamma_v}$, calculated from the work of PRINS et al., is given in the following table.

Table 1.

$4\,\dfrac{hD}{\delta\,\Gamma_v}$	$\dfrac{\Phi_m}{2\pi r\,(C^* - C_0)\,\Gamma_v}$
0·01	0·025
0·02	0·040
0·05	0·075
0·10	0·120

2. DESCRIPTION OF EQUIPMENT

The equipment has been described in detail in [1]. The chief modification for the purposes of this paper was the introduction of the water through a narrow slit at the top of the column. A

second alteration was the addition of a plastic cover to the liquid receiver. The liquid in the receiver was kept in contact with the cover during a run so that the surface exposed to the SO_2 was greatly reduced. A sketch of the absorber, showing the changes mentioned, is given in Fig. 1. For further details of the equipment the reader is referred to [1].
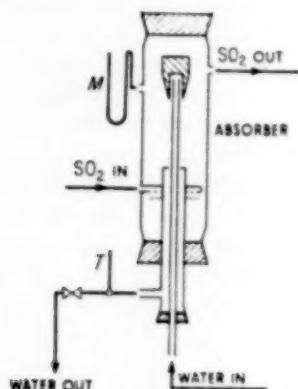
Fig. 1. Sketch of modified absorber.

3. Treatment of Data

The data were reduced to the common basis of a partial pressure of SO_2 of 750 mm Hg and a surface temperature of the water film of 20°C. The manner in which these adjustments were made has been described in [1]. In all experiments pure (99·9%) SO_2 was absorbed in distilled water. In some cases a surface-active agent (*Teepol*) was added. The height of the band of ripples was measured with a millimetre scale mounted inside the absorber with a precision of about half a millimetre. This measurement was made while gas was being absorbed.

4. Discussion of Results

Gas absorption measurements were made at column heights of 5, 3, 2, and 1 cm using pure water and dilute solutions of *Teepol* of various concentrations. These data are plotted in Fig. 2 as Φ_m versus $\Gamma_v^{\frac{1}{3}}$. For comparison, equation (2), with $h_r = 0$, has been drawn in for the four column heights, and equation (3) has been drawn in for a height of 2 cm. The values of C^* and D

used were taken from [1]. For the shorter columns equation (2) was drawn in only for values of $\Gamma_v^{\frac{1}{3}}$ above $1\cdot2 \left[\dfrac{cm^3}{cm\ sec.}\right]^{\frac{1}{3}}$ to avoid confusion with regard to which points should approach which lines.

1 EQ. (2) FOR $h_r = 5\cdot0$ cm
2 EQ. (2) FOR $h_r = 3\cdot0$ cm
3 EQ. (2) FOR $h_r = 2\cdot0$ cm
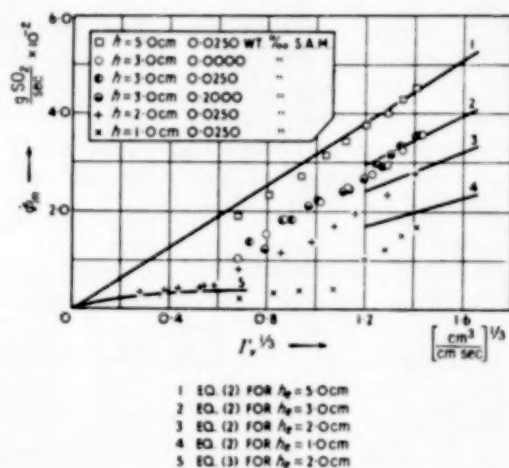4 EQ. (2) FOR $h_r = 1\cdot0$ cm
5 EQ. (3) FOR $h_r = 2\cdot0$ cm

Fig. 2. Rates of absorption for different heights of column as functions of flow rate.

In Fig. 2 the effect of the stagnation of the surface of the film below the band of ripples is quite apparent. As the flow rate increases, the height of the band of ripples decreases, and the measured rate of absorption approaches the calculated rate.

The height of the end-effect is not affected by the height of the column (see Fig. 3). For this reason the fraction of the total area of the column which is below the band of ripples at a given liquid flow rate will be greater for the shorter columns. This is reflected in the rate of absorption, as shown in Fig. 2. The deviation of the points from the theoretical lines shows a consistent increase as the column height decreases.

Various *Teepol* concentrations were used with the 3-cm column. It is seen that, within the experimental error, there is no observable effect of the addition of the *Teepol*.

For both the 1- and the 2-cm columns the band of ripples reaches the top of the column at a

certain flow rate below which the entire surface of the film appears to be nearly stagnant. The absorption data for the two columns show distinct breaks at those flow rates.

Absorption data for the 2-cm column were taken at exceptionally low flow rates, in the region where the entire column is covered with the stagnant film. As seen in Fig. 2, the points lie consistently 15 to 20% above the curve of equation (3). It is interesting, however, that the agreement is as good as this considering the assumptions involved in the derivation of the equations.

In Fig. 3 is a plot of $\sqrt{h_r}$ versus $\Gamma_v^{\frac{1}{3}}$. It is seen that the height of the end-effect does not depend upon the height of the column, but is influenced by the *Teepol* concentration. As *Teepol* is added, the band of ripples becomes fainter and more difficult to observe. At low *Teepol* concentrations h_r is somewhat greater than with water, while at high *Teepol* concentrations it is appreciably lower. As mentioned before, however, the addition of the *Teepol* had no measurable effect on the gas absorption. For this reason, the line shown in Fig. 3 was drawn through the points for water without regard to the points for the *Teepol* solutions.

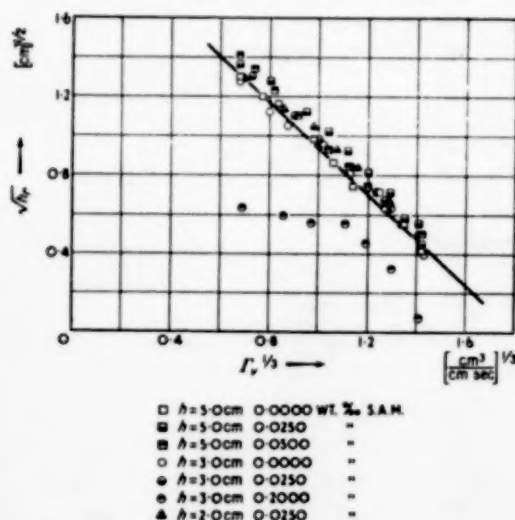The straight line in Fig. 3 was used to correlate the data for various columns in Fig. 4, where Φ_m is plotted versus $\Gamma_v^{\frac{1}{3}}(h-h_r)^{\frac{1}{2}}$. Equation (2) is again drawn in the figure, and it is seen that the correlation is remarkably good. From the agreement of the data with the calculated line
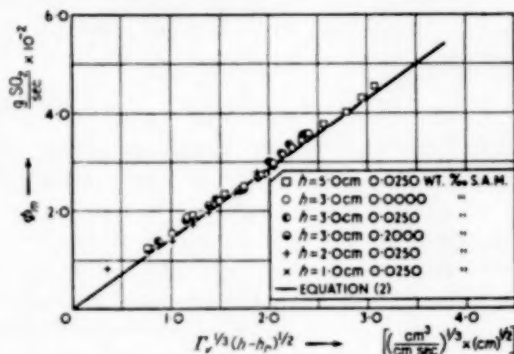
Fig. 4. Correlation of rates of absorption for different columns by subtracting stagnant area.

it must be concluded that the stagnant lower part of the film indeed absorbs gas at a greatly reduced rate.

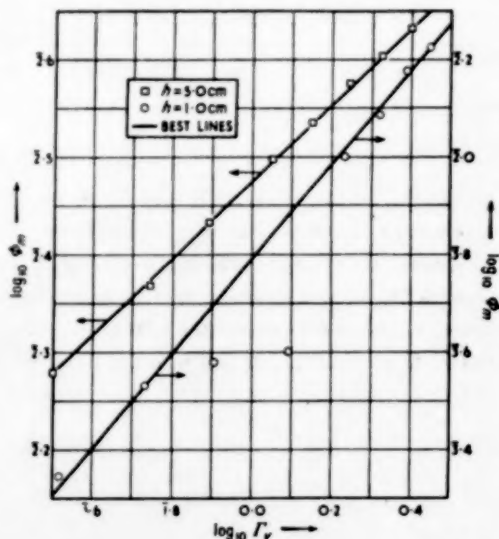In Fig. 5 the data for the 1-cm and the 5-cm columns are plotted on a log-log scale to show

Fig. 3. Height of the end-effect as a function of flow rate.

Fig. 5. Log-log plot of absorption data to demonstrate weakness of this form of presentation.

61

the interpretation that one might be led to from such a presentation. The points for the 5-cm column lie on a rather nice straight line having a slope of 0·39. If one discards two of the points for the 1-cm column, the other six form a line with a slope of 0·97. The data for the other columns can be plotted similarly to obtain values for the exponent n in the equation

$$\Phi_m \sim \Gamma_v^n \qquad (4)$$

which lie between the two mentioned above. It is possible that the presence of stagnant regions on the liquid films flowing in packed columns is responsible for the well-known facts that the exponent in equation (4) is usually about twice the value of $1/3$ predicted by the penetration theory, and that the value of this exponent depends upon packing shape and size and the nature of the absorbing liquid.

The presence of such stagnant regions can be demonstrated by introducing lycopodium powder into a laboratory-size packed column. Whirling groups of powder particles can then be seen, and the residence time of the powder in the column is found to be far greater than that of the liquid.

5. Discussion of Errors

The work presented in this article is subject to the same errors and uncertainties discussed in [1]. Because the rate of gas absorption by the short columns is smaller than by the long columns,

the percentage deviation of the experimental points from a smooth curve drawn through them is somewhat greater in this work.

6. Limits of Applicability

The conditions studied here were for column heights between 1 and 5 cm and for Reynolds' numbers between 20 and 1150. This corresponds to contact times between 0·01 and 0·22 seconds neglecting the stagnation effect.

Acknowledgment

Notation

A = area of film surface, cm^2
C_0 = initial concentration of solute in bulk of liquid, g/cm^3
C^* = concentration of solute in saturated solution, g/cm^3
D = diffusivity of solute in liquid, cm^2/sec
g = acceleration due to gravity, $981\ cm/sec^2$
h = height of column, cm
h_r = height of band of ripples, cm
h_e = effective height of column $(h - h_r)$, cm
r = radius of tube, cm
Re = Reynolds' number of film
t_e = contact time of an element of area in the column, sec
Γ_v = volumetric rate of flow per centimetre, $\dfrac{cm^3}{cm/sec}$
δ = thickness of liquid film on wall of column, cm
ν = kinematic viscosity, cm^2/sec
Φ_m = rate of absorption, g/sec

References

[1] Lynn, S., Straatemeier, J. R. and Kramers, H.; Chem. Eng. Sci. 1955 4 49.

[2] Matsuyama, T.; Mem. Fac. Eng. Kyoto University, 1953 15 142.

[3] Peaceman, D. W.; Sc.D. Thesis, Chem. Eng. M.I.T., 1951.

[4] Emmert, R. E. and Pigford, R. L.; Chem. Eng. Prog. 1954 50 87.

[5] Lynn, S.; Trans Inst. Chem. Engrs. (London) 1954 32 S75.

[6] Prins, J. A., Mulder, J. and Schenk, J.; Appl. Sci. Res. 1951 A2 431.

Absorption studies in the light of the penetration theory

III. Absorption by wetted spheres, singly and in columns

S. Lynn, J. R. Straatemeier and H. Kramers

Laboratorium voor Physische Technologie, Technische Hogeschool, Delft

Summary—A study has been made of the absorption of SO_2 by water flowing in a laminar film over the surface of single spheres and columns of spheres. By means of the penetration theory it is possible to correlate the data for spheres of radii from 1 to 3 cm, and for columns containing up to fourteen spheres. It appears that there is little or no mixing of the surface layers with the bulk of the liquid as it flows from one sphere to the next in a vertical row.

Résumé—On a étudié l'absorption de SO_2 par eau, qui coule en couche laminaire sur la surface d'une sphère et d'une colonne formée par sphères superposées. Il a paru possible de trouver une correlation satisfaisante entre la vitesse d'absorption et la dimension des sphères (2 à 6 cm. diamètre), leur nombre (1 à 14) et le debit d'eau (0·5 à 7·5 cm³/sec). Cette correlation peut être prédite au moyen de la theorie de diffusion non-stationnaire. Les expériences démontrent qu'il ne se produit pas un melange entre la surface et l'intérieur du liquide quand celui-ci passe d'une sphère à l'autre.

1. Introduction

In the first article of this series [1] it was found that for physical absorption without gas phase resistance in a wetted-wall column the simple theory of transient diffusion into a stagnant layer of liquid (penetration theory) is valid for contact times up to 1 second. In the case of a film of liquid flowing over a sphere a similar mathematical treatment is greatly complicated if one attempts to consider the stretching of the film, and the consequent distortion of the concentration gradients, as it flows from the top of the sphere to the bottom. This stretching will have the effect of increasing the concentration gradients on the upper half of the sphere and of decreasing them on the lower half. Because the film on the upper half of the sphere, being fresher, absorbs faster than when it is on the lower half, one would expect the net effect of the stretching and contracting of the film to be an increased rate of absorption. Without considering these effects, the following calculation can be made :

Consider a sphere of radius R (cm) with an angular coordinate α which is zero at the top of the sphere and π at the bottom. Liquid flows over the sphere in a laminar film, with a total volumetric flow rate of Φ_v (cm³/sec). It is assumed that the thickness of the film, δ, at any latitude on the sphere is the same as it would be for the same flow rate per unit length, Γ_v (cm³/cm-sec), on a plane surface making the same angle with the vertical. Thus :

$$\delta = \sqrt[3]{\frac{3\,\nu\,\Gamma_v}{g\sin\alpha}}$$
$$= \sqrt[3]{\frac{3\,\nu\,\Phi_v}{2\,\pi\,R\,g\sin^2\alpha}}, \qquad (1)$$

where ν = kinematic viscosity, cm²/sec

g = acceleration due to gravity, 981 cm/sec².

It follows from the above assumption that a half-parabolic velocity profile will exist at all latitudes on the sphere, so that the velocity of the surface of the film, v_i (cm/sec), is given by the following equation :

$$v_i = \frac{3}{2}\frac{\Gamma_v}{\delta}$$
$$= \left(\frac{9\,g}{32\,\nu\,\pi^2}\right)^{1/3}\Phi_v^{\,2/3}R^{-2/3}\sin^{-1/3}\alpha. \qquad (2)$$

The rate of absorption of a differential unit of area on the film is

$$d\,\Phi_m = (C^\bullet - C_0)\sqrt{\frac{D}{\pi t}}\,dA, \qquad (3)$$

where Φ_m = rate of gas absorption, g/sec

$C^\bullet$ = concentration of solute in saturated solution, g/cm^3

C_0 = initial concentration of solute in bulk of liquid, g/cm^3

D = diffusivity of solute in liquid, $cm^2/$sec

t = time during which the element of area has been exposed to the gas, sec

The "age" of an element of area at latitude α is

$$t = \int_0^\alpha \frac{R\,d\alpha}{v_i}$$

$$= \left(\frac{32\,\nu\,\pi^2}{9\,g}\right)^{\frac{1}{3}}\Phi_v^{-2/3}\,R^{5/3}\int_0^\alpha \sin^{1/3}\alpha\,d\alpha$$

and an element of area can be expressed as

$$dA = 2\pi\,R^2\sin\alpha\,d\alpha.$$

Thus, the rate of absorption for the whole sphere becomes

$$\Phi_m = (C^\bullet - C_0)\,\sqrt{D}\left(\frac{18\,g\,\pi}{\nu}\right)^{1/6}\Phi_v^{1/3}\,R^{7/6}$$

$$\int_0^\pi \frac{\sin\alpha\,d\alpha}{\left[\int_0^\alpha\sin^{1/3}\alpha\,d\alpha\right]^{1/2}}. \qquad (4)$$

The value of the term

$$\int_0^\pi \frac{\sin\alpha\,d\alpha}{\left[\int_0^\alpha\sin^{1/3}\alpha\,d\alpha\right]^{\frac{1}{2}}} \qquad \text{is } 2\cdot 33$$

and the value of

$$\int_0^\pi \sin^{1/3}\alpha\,d\alpha \qquad \text{is } 2\cdot 58, \text{ as}$$

determined by numerical integration.

For the absorption of SO_2 in water when the partial pressure of the SO_2 is 750 mm Hg and the temperature of the surface of the water film is 20°C, equation (4) can be expressed as

$$\Phi_m = K\,R^{7/6}\,\Phi_v^{1/3}. \qquad (4a)$$

The value of K obtained using the values of the pertinent physical properties listed in [1] is $1\cdot 19 \times 10^{-2}$ [g SO_2/sec $cm^{-7/6}$ (cm^3 H_2O/sec$)^{-1/3}$]. This value can only be considered as an approximation because the flow conditions at the top and bottom of the sphere have been idealized and the effect of the stretching and contracting of the film has been disregarded.

The derivation above has been for single spheres. For spheres mounted in a column one must consider whether the streamlines of the flowing film are effectively mixed as the liquid passes from one sphere to the next. As has been shown above, the rate of absorption in the case of one sphere is

$$\Phi_m \sim (C^\bullet - C_0)\,\frac{A}{\sqrt{t_c}}$$

where t_c is the time in which an element of area is exposed to the gas in moving from the top of the sphere to the bottom. If there is complete mixing of the streamlines of the fluid at the points between the spheres, and if the concentration of the dissolved gas in the outgoing liquid is small relative to $C^\bullet$, the rate of absorption for N spheres will be approximately :

$$[\Phi_m]_{N\,\text{spheres}} \cong N\cdot[\Phi_m]_{1\,\text{sphere}}$$

If there is no mixing of the streamlines in the flow from one sphere to the next, the contact time for the liquid flowing down a row of N spheres will be $N\cdot t_c$, the total area exposed to the gas will be $N\cdot A$, and the rate of gas absorption will be

$$[\Phi_m]_{N\,\text{spheres}} = \sqrt{N}\cdot[\Phi_m]_{1\,\text{sphere}}$$

or from equation (4a),

$$\Phi_m = K\,\sqrt{N}\,R^{7/6}\,\Phi_v^{1/3}. \qquad (5)$$

It should be remembered that the derivation of these equations rests on the assumption that film can be considered as a semi-infinite medium. With other words, the "depth of penetration"

of the solute must be small, and the relative saturation of the outgoing liquid will be low.

2. DESCRIPTION OF EQUIPMENT

The equipment used was the same as that described in [1] and [2] except that the absorber was modified to permit the placement of the spheres, as shown in Fig. 1. Single spheres having
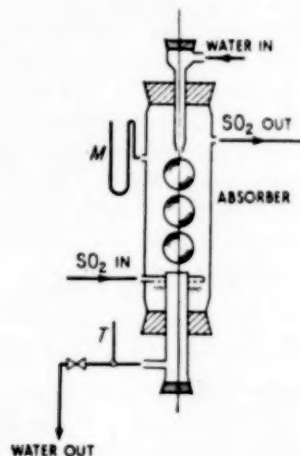

FIG. 1. Sketch of modified absorber.

radii of 1·00, 1·50, 1·90, and 2·95 cm were used. Vertical rows of 3, 5, 10, and 14 spheres having radii of 1·00 cm were also studied. The bottom of the lowest sphere was set 2 cm above the level of the liquid in the receiver to minimize the influence of the end-effect described in [2]. The liquid receiver was equipped with a plastic cover, also described in [2]. For further details of the equipment the reader is referred to [1].

3. TREATMENT OF DATA

The data were reduced to the common basis of a partial pressure of SO_2 of 750 mm Hg and a surface temperature of the water film of 20°C. The manner in which these adjustments were made has been described in [1]. In all experiments pure (99·9%) SO_2 was absorbed in distilled water to which a surface-active material (*Teepol*) had been added. The spheres were made from steel ball-bearings and were mounted on a stainless steel rod.

The results presented here are subject to the same errors and uncertainties discussed in [1] and [2]. The average deviation of the points in Fig. 2 from the solid line is $0·11 \times 10^{-2}$ g SO_2/sec.

4. DISCUSSION OF RESULTS

The rate of absorption using single wetted spheres is shown in Fig. 2, plotted against $\sqrt{N} R^{7/6} \Phi_v^{1/3}$. The slope of the solid line through the points is about 7·6% greater than the value of K calculated
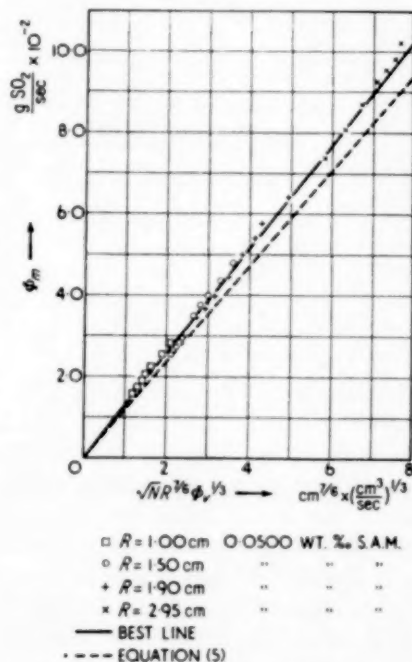
FIG. 2. Gas absorption by single spheres.

from the penetration theory. This disagreement is probably due to the stretching effect, which was neglected in the derivation of equation (5), and is actually smaller than might have been expected. Of more importance is that the data for the four spheres all fall on the same straight line when plotted in the manner suggested by the penetration theory.

The solid line of Fig. 2 is also drawn in Fig. 3, where it is seen to represent the data for vertical rows containing up to 14 spheres with good precision at sufficiently low flow rates. It is seen
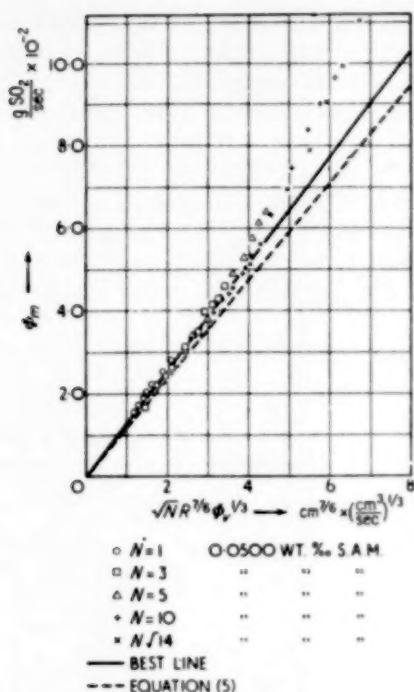
FIG. 3. Gas absorption by columns of spheres, $R = 1 \cdot 00$ cm

that the data for the 5-sphere column begin to deviate appreciably from the solid line at a flow rate of $4 \cdot 2$ cm^3/sec. Those for the 10-sphere column begin to deviate at $2 \cdot 0$ cm^3/sec, and those for the 14-sphere column begin to deviate at $1 \cdot 9$ cm^3/sec. This effect is due to the increasingly great tendency of the liquid film to ripple at a given liquid flow rate as the number of spheres in the column is increased. The instability of the flow over the lower spheres in a column is observed as a tendency for the liquid stream to " dance " back and forth at the points where the spheres are joined to each other. This tendency is decreased, but not eliminated, by the addition of $0 \cdot 050$‰ of a surface-active material (*Teepol*). With concentrations of *Teepol* either greater or less than this the tendency to ripple is greater.

The fact that the data for the columns of spheres fall on a straight line when plotted in the manner of Fig. 3 is a strong indication that there is essentially no mixing of the streamlines in the film as it flows from one sphere to the next.

These results suggest that liquid in laminar flow in a packed column may frequently travel over many pieces of packing before effective mixing of the surface layers and the bulk of the liquid occurs. The average liquid-side resistance to absorption would then be greater than if mixing were taking place at each juncture between the pieces of packing. However, as has been indicated in [2], at the places where such mixing does occur, there is a stagnant surface over the region one to two cm above the point of mixing, again resulting in a reduction of the absorption rate. In the practical case, the effects described in this paper and in [2] are counteracted by turbulent regions in the film, which are produced by local uneven wetting of the packing and by the stream of gas. This turbulence tends to decrease the liquid-side resistance.

5. Limits of Applicability

The conditions studied here were for single spheres with radii between $1 \cdot 00$ and $2 \cdot 95$ cm, for columns containing up to 14 spheres having radii of $1 \cdot 00$ cm and for flow rates between $0 \cdot 5$ and $7 \cdot 5$ cm^3 H$_2$O/sec. This corresponds to contact times between $0 \cdot 29$ and $0 \cdot 05$ sec for the 1 cm-radius sphere and between $1 \cdot 78$ and $0 \cdot 29$ sec for the 3 cm-radius sphere.

Notation

A = area of sphere, cm^2

C^* = concentration of solute at saturation, g/cm^3

C_0 = initial concentration of solute in bulk of liquid, g/cm^3

D = diffusivity of solute in liquid, cm^2/sec

g = acceleration due to gravity, 981 cm/sec^2

K = constant in equation (4a)

N = number of spheres in a column

R = radius of sphere, cm

t = time of contact with gas of an element of area, sec

t = time of contact with gas of an element of area in moving over one sphere, sec

v_i = velocity of surface of film, cm/sec

α = angular coordinate on sphere

Γ_v = liquid flow rate per unit length, cm^3/cm sec

δ = film thickness, cm

ν = kinematic viscosity, cm^2/sec

Φ_m = rate of absorption of gas, g/sec

Φ_v = liquid flow rate, cm^3/sec

REFERENCES

[1] LYNN, S., STRAATEMEIER, J. R. and KRAMERS, H.; *Chem. Eng. Sci.* 1955 **4**, 49.

[2] LYNN, S., STRAATEMEIER, J. R. and KRAMERS, H.; *Chem. Eng. Sci.* 1955 **4** 58.

On the steady state fractionation of multicomponent and complex mixtures in an ideal cascade

Part 2.—The calculation of the minimum reflux ratio

Andreas Acrivos* and Neal R. Amundson**

Department of Chemical Engineering, University of Minnesota, Minnneapolis 14, Minnesota

Summary - The important problem of calculating the minimum reflux ratio in the separation of multicomponent and complex mixtures in an ideal cascade has been solved in closed form. The solution of two rather unusual integral equations may be of interest. Numerical calculations have been performed and will be reported elsewhere.

Resumé—Les auteurs ont résolu le problème important du calcul du rapport du reflux minimum dans la séparation d'un mélange de composants multiples et complexes, dans le cas d'une cascade idéale.

La solution de deux équations intégrales assez particulières peut être intéressante.

Les calculs numériques ont été faits et seront présentés dans un autre texte.

5. Introduction

In a previous article the authors examined theoretically the fractionation of multicomponent and complex mixtures in an ideal cascade and solved the equations, describing the process, in a closed form. The object of such a calculation is the following. Given a mixture of known composition and thermal condition it is desired to determine the number of stages in the enriching and stripping sections of the cascade to separate the feed into two streams such that $x_0(\beta)$ and $x_0(\beta^*)$ are specified *a priori*. Here β and β^* are two components and $x_0(j)$ is the mole fraction of the jth component in the product streams. However, the final answer depends on two additional parameters, the feed stage location and the reflux ratio R. One introduces the feed at such a location to minimize the total number of stages required for the specified separation. It is found that as the reflux ratio is decreased the number of plates in both sections of the column, N and S, increase until a value of R is reached for which both N and S are essentially infinite, even with the optimum feed stage location. Since in an actual operation $R > R_{\min}$ the calculation of this minimum reflux ratio for any desired separation is of considerable importance.

Exact methods for determining $R_{\min}$ in an ideal cascade have been worked out recently for discrete mixtures by Underwood [1] and Murdoch and Holland [2]. In this paper the formulae of Murdoch and Holland will be derived in a somewhat more general form, and these will be generalized to the complex mixtures when the number of components in the mixture becomes infinite.

6. Minimum Reflux for Discrete Mixtures

Equation (3.19) with $p_i^* = p_i$ may be written

$$\frac{x_0(i)}{x_0^*(i)} \frac{R^*}{R} =$$

$$\frac{\sum\limits_{k=1}^{m} \phi_k^{-S-1} \dfrac{C_k^*}{p(i) - \phi_k}}{\sum\limits_{k=1}^{m} \lambda_k^{N-1} \dfrac{C_k}{\lambda_k - p(i)}} \cdot \frac{\sum\limits_{k=1}^{m} C_k \lambda_k^{N-1}}{\sum\limits_{k=1}^{m} C_k^* \phi_k^{-S-1}} \quad (6.1)$$

* Department of Chemistry and Chemical Engineering, University of California, Berkeley, California.

** On leave at Dept. of Chem. Eng., Cambridge University, Cambridge, England.

Let the two functions

$$G_k = \frac{C_k}{C_h} \left(\frac{\lambda_k}{\lambda_h}\right)^{N-1} \qquad (6.2)$$

$$G_k^* = \frac{C_k^*}{C_l^*} \left(\frac{\phi_l}{\phi_k}\right)^{S+1} \qquad (6.3)$$

be defined where l and h are arbitrary for the moment save that $1 \leq h, l \leq m$. Then (6.1) can be written

$$\frac{x_0(i)}{x_0^*(i)} \frac{R^*}{R} = Z \frac{\sum\limits_{k=1}^{m} \dfrac{G_k^*}{p(i) - \phi_k}}{\sum\limits_{k=1}^{m} \dfrac{G_k}{\lambda_k - p(i)}} \qquad (6.4)$$

and

$$Z = \frac{\sum\limits_{k=1}^{m} G_k}{\sum\limits_{k=1}^{m} G_k^*}$$

Now the numbers λ_k, $1 \leq k \leq m$, are the m roots of the characteristic equation (3.7), i.e.,

$$\sum_{j=1}^{m} \frac{p(j)\,x_0(j)}{\lambda_k - p(j)} = R \qquad (6.5)$$

and therefore one can say

$$\Gamma(\lambda) =$$
$$\prod_{k=1}^{m} (\lambda - p(i)) \left\{ R - \sum_{j=1}^{m} \frac{p(j)\,x_0(j)}{\lambda - p(j)} \right\} = R \prod_{i=1}^{m} (\lambda - \lambda_i)$$

From this it follows that if $\lambda = p(i)$ then[*]

$$\frac{p(i)\,x_0(i)}{R} = \frac{\prod\limits_{k=1}^{m} (\lambda_k - p(i))}{\prod\limits_{k=1}^{m} {}'(p(k) - p(i))} \qquad (6.6a)$$

Similarly

$$\frac{p(i)\,x_0^*(i)}{R^*} = \frac{\prod\limits_{k=1}^{m} (p(i) - \phi_k)}{\prod\limits_{k=1}^{m} {}'(p(i) - p(k))} \qquad (6.6b)$$

Finally if r_j, $i \leq j \leq m-1$, are the $m-1$ finite roots of

$$\sum_{k=1}^{m} \frac{G_k}{\lambda_k - r_j} = 0 \qquad (6.7a)$$

___

[*] π, indicates an obvious term must be omitted from the product.

it can be shown that

$$\sum_{k=1}^{m} \frac{G_k}{\lambda_k - p} = \frac{\prod\limits_{j=1}^{m-1} (r_j - p)}{\prod\limits_{k=1}^{m} (\lambda_k - p)} \sum_{k=1}^{m} G_k \qquad (6.8a)$$

and

$$\sum_{k=1}^{m} \frac{G_k^*}{p - \phi_k^*} = \frac{\prod\limits_{j=1}^{m-1} (p - r_j^*)}{\prod\limits_{k=1}^{m} (p - \phi_k)} \sum_{k=1}^{m} G_k^* \qquad (6.8b)$$

where r_j^*, $1 \leq j \leq m-1$, are the $m-1$ finite roots of

$$\sum_{k=1}^{m} \frac{G_k^*}{r_j^* - \phi_k} = 0 \qquad (6.7b)$$

Therefore if the above equations are substituted into (6.4) it is found that

$$\prod_{k=1}^{m-1} (r_k - p_i) = \prod_{k=1}^{m-1} (r_k^* - p_i), \ 1 \leq i \leq m$$

and hence

$$r_k = r_k^* \qquad 1 \leq k \leq m-1 \qquad (6.9)$$

The function G_k will now be examined for large N. By definition

$$p(m) < p(m-1) < ---- < p(i)$$

and

$$p(k) < \lambda_k < p(k-1)$$

Hence if it is assumed that $C_h \neq 0$, then since

$$G_k = \frac{C_k}{C_h} \left(\frac{\lambda_k}{\lambda_h}\right)^{N-1}$$

it follows that as $N \to \infty$

(a) $G_k \to 0$, $k > h$

(b) $G_h \to 1$ by definition

(c) G_k exists for $k < h$ only if $\lim\limits_{N \to \infty} C_k \left(\dfrac{\lambda_k}{\lambda_h}\right)^N$ exists.

But this implies that for $k < h$, $C_k \to 0$ as $N \to \infty$ and therefore

$$C_k \to \frac{p(k)\,x_0(k)}{[\pi(k)]^2}$$

Hence it is included that G_k, $k < h$, exists, if and only if

$$\lim_{N \to \infty} x_0(k) \left(\frac{\lambda_k}{\lambda_h}\right)^N \qquad (6.10)$$

exists. Moreover, it is seen that as $N \to \infty$ the function $x_0(i)$ can be separated into two distinct parts such that

(a) $x_0(i) \neq 0$, $i \geq h$

(b) $x_0(i) \to 0$, $i < h$, as $N \to \infty$ in such a way that

$$\lim_{N \to \infty} x_0(i) \left(\frac{\lambda_i}{\lambda_h}\right)^N$$

exists. Similarly

(a) $x_0^*(i) \neq 0$, $i \leq l$

(b) $x_0^*(i) \to 0$, $i > l$, as $S \to \infty$ in such a way that

$$\lim_{S \to \infty} x_0^*(i) \left(\frac{\phi_l}{\phi_i}\right)^S$$

exists and $G_k^* \to 0$ for $k \geq l$, while $G_k^* \neq 0$, for $k \geq l$ as $S \to \infty$.

It follows then from (6.7a), (6.7b), and (6.9) that as $N \to \infty$, $S \to \infty$

(a) $r_{k-1} \to \lambda_k$, $k \gg h + 1$

(b) $r_k \to \phi_k$, $k \leq l - 1$

and, therefore, at minimum reflux

$$\lambda_k = \phi_{k-1} \qquad h + 1 \leq k \leq l \qquad (6.11)$$

The above result was first derived rigorously by MURDOCH and HOLLAND [2] although it had been anticipated earlier by UNDERWOOD [1].

However, the two characteristic equations from which λ_k and ϕ_k are calculated are

$$\sum_{j=1}^{m} \frac{p(j) x_0(j)}{\lambda_k - p(j)} = \frac{L}{D} \text{ and } \sum_{j=1}^{m} \frac{p(j) x_0^*(j)}{p(j) - \phi_k} = \frac{L^*}{W}$$

and since

$$Dx_0(j) + Wx_0^*(j) = x_F(j) \qquad (6.12)$$

where $x_F(j)$ represents the mole fraction of the jth component in the feed, it follows from the above and from (6.11) that

$$\sum_{j=1}^{m} \frac{p(j) x_F(j)}{\lambda_k - p(j)} = -q \cdot h + 1 \leq k \leq l \qquad (6.13)$$

The parameter $q = L^* - L$ can be calculated

from a knowledge of the thermal condition of the feed.

It is seen then that $(l - h)$ characteristic roots λ_k, $(h + 1) \leq \lambda_k \leq l$ can be determined from (6.13) without a knowledge of the function $x_0(j)$. Also, since $x_0^*(j) = 0$ for $j > l$, it follows from (6.11) that

$$Dx_0(j) = x_F(j) \quad . \quad j > l \qquad (6.14)$$

Now the characteristic equation for the enriching section of the cascade is

$$\sum_{j=h+1}^{l} \frac{p(j) D x_0(j)}{\lambda_k - p(j)} = RD - \sum_{j=l+1}^{m} \frac{p(j) D x_0(j)}{\lambda_k - p(j)} \qquad (6.15)$$

since $x_0(j) = 0$ for $j < h$.

Next two functions A_k and $B(k)$ are defined such that

$$\sum_{k=h+1}^{l} \frac{A_k}{\lambda_k - p(i)} = 1 \quad , \quad h + 1 \leq i \leq l \qquad (6.16)$$

and

$$\sum_{k=k+1}^{l} \frac{B(k)}{\lambda_i - p(k)} = 1 \quad , \quad h + 1 \leq i \leq l \qquad (6.17)$$

It can be shown easily that

$$\sum_{k=k+1}^{l} \frac{A_k}{(\lambda_i - p(i))(\lambda_k - p(j))} = \begin{cases} 0 & i \neq j \\ \frac{1}{B(i)} & i = j \end{cases}$$
$$h + 1 \leq i, j \leq l \qquad (6.18)$$

and, moreover, that

$$B(i) = \frac{\prod\limits_{k=h+1}^{l} (\lambda_k - p(i))}{\prod\limits_{k=h+1}^{l} (p(k) - p(i))} , h + 1 \leq i \leq l \qquad (6.19)$$

So by multiplying (6.15) through by $A_k/(\lambda_k - p(i))$ and summing on k there results, because of (6.18) and (6.14)

$$p(i) D x_0(j) = B(i) \left\{ RD - \frac{p(h) D x_0(h)}{B(h)(p(i) - p(h))} \right.$$
$$\left. - \sum_{j=l+1}^{m} \frac{p(j) x_F(j)}{B(j)(p(i) - p(j))} \right\} \qquad (6.20)$$

for $h + 1 \leq i \leq l$ where

$$B(i) = \frac{\prod\limits_{k=h+1}^{l} (\lambda_k - p(i))}{\prod\limits_{k=h+1}^{l} (p(k) - p(i))}$$
$$i = h \text{ and } i \geq l + 1 \qquad (6.19a)$$

In this manner $(l - h)$ linearly independent non-homogeneous linear simultaneous equations in $(l - h)$ unknowns have been solved. It must be kept in mind that λ_k, $h + 1 \leq k \leq l$, and $B(i)$ can be calculated *a priori* from the known composition and thermal condition of the feed. Hence from (6.20), from

$$\sum_{j=h}^{m} D x_0(j) = D \qquad (6.21)$$

and the fact that $x_0(\beta)$ and $x_0(\beta^*)$, where $h \leq \beta$, $\beta^* \leq l$ are specified, one can calculate both the complete composition of the overhead product and the minimum reflux ratio. Of course, it must be understood that h and l are not known *a priori*, and so, in general, there are more unknowns than there are equations. However, it turns out, in all the cases which have been investigated so far, that the system of equations (6.20) and (6.21) has only one solution which satisfies the additional requirement

$$0 < D x_0(i) < x_F(i) \quad \text{for} \quad h \leqslant i \leqslant l \qquad (6.22)$$

In practice it is best to assume h and l first, and then to solve equation (6.20). This process is repeated until (6.22) is obeyed.

The solution to the minimum reflux problem is exact. It is desired now to develop the analogous results for complex mixtures.

7. Minimum Reflux for Complex Mixtures

1. *Continuous mixtures.* By definition the distribution function of a continuous mixture is single valued and continuous and it will be supposed that $x_0(p)$, the distribution function of the overhead product, does not vanish along the positive p axis. Therefore from (4.26)

$$x_N(p) = \frac{p \, x_0(p)}{R} \cdot$$

$$\frac{P \int_0^\infty \lambda^{N-1} \dfrac{C(\lambda)}{\lambda - p} \, d\lambda + \dfrac{p^{N-1} C(p)}{p \, x_0(p)} \, w(p)}{\int_0^\infty \lambda^{N-1} C(\lambda) \, d\lambda} \qquad (7.1)$$

Or, if the new function $G(\lambda)$ is defined

$$G(\lambda) = \frac{C(\lambda)}{C(h)} \left(\frac{\lambda}{h}\right)^{N-1} \qquad (7.2)$$

where h is, thus far, arbitrary, then

$$x_N(p) = \frac{p \, x_0(p)}{R} \cdot$$

$$\frac{P \int_0^\infty \dfrac{G(\lambda)}{\lambda - p} \, d\lambda + \dfrac{G(p)}{p \, x_0(p)} \, w(p)}{\int_0^\infty G(\lambda) \, d\lambda} \qquad (7.3)$$

Now as $N \to \infty$, it follows from (3.2) that if $C_h \neq 0$

(a) $G(\lambda) \to 0, \quad \lambda < h$

(b) $G(h) = 1$

(c) $G(\lambda)$, $\lambda > h$, exists only if $\lim_{N \to \infty} \left(\dfrac{C(\lambda)}{C(h)}\right) \left(\dfrac{\lambda}{h}\right)^N$ exists.

But, according to the definition of $C(\lambda)$

$$C(\lambda) = \frac{\lambda \, x_0(\lambda)}{[w(\lambda)]^2 + [\pi \lambda x_0(\lambda)]^2} \qquad (7.4)$$

and therefore it may be concluded that $G(\lambda)$ for $\lambda > h$ exists only if

$$\lim_{N \to \infty} \frac{x_0(\lambda)}{x_0(h)} \left(\frac{\lambda}{h}\right)^N \qquad (7.5)$$

exists.

Some complications arise, however, because as N becomes large and is made formally to approach infinity, one obtains from (7.3)

$$\lim_{N \to \infty} x_0(h) \, P \int_0^\infty \frac{G(\lambda)}{\lambda - h} \, d\lambda \qquad (7.5a)$$

should exist which implies that $x_0(h)$ and therefore $C(h)$ approach zero as $N \to \infty$. In spite of this, it can be rigorously shown that

$$\lim_{N \to \infty} G(\lambda) = 0 \quad , \quad \lambda < h.$$

Thus, at minimum reflux the distribution function of the overhead product, $x_0(p)$, can be separated into two distinct parts, such that

(a) $x_0(p) \neq 0, \quad p < h$

(b) $x_0(p) \to 0$, $p > h$, according to (7.5)

while $x_0(h)$ approaches zero according to (7.5a). Similarly the distribution function $x_0^*(p)$ can be separated into two distinct parts, such that

(a) $x_0^*(p) \neq 0$, $p > l$

(b) $x_0^*(p) \to 0$, $p < l$, in such a way that

$$\lim_{s \to \infty} \frac{x_0^*(p)}{x_0^*(l)} \left(\frac{l}{p}\right)^s \qquad (7.5b)$$

exists.

To solve the problem for continuous mixtures, one sub-divides the interval $0 < p \leq a$, where a is arbitrary, but large, into m equal parts, Δp, and determines the asymptotic form of the solution for the discrete problem as $\Delta p \to 0$. The limiting form of (6.13) is

$$P \int_0^\infty \frac{p\,x_p(p)}{\lambda - p} dp + \lambda\,x_p(\lambda)\,\pi \cot \pi \rho(\lambda) = -q \quad (7.6)$$

for $l \leq \lambda < h$, an equation which defines a function $\rho(\lambda)$, $l \leq \lambda < h$, which is identical for, $l \leq \lambda < h$, with the function $\rho(\lambda)$ defined by

$$P \int_0^\infty \frac{p x_0(p)}{\lambda - p} dp + \lambda\,x_0(\lambda)\,\pi \cot \pi \rho(\lambda) = R \quad (7.6a)$$

On the other hand (6.19) becomes

$$B(i) = \rho(i) \mathop{\pi}_{k=1}^{m_1} \cdot \left(1 + \frac{\rho(k)}{k-i}\right)$$

where $m_1 = \dfrac{h-l}{\Delta p}$, or

$$\ln B(i) = \ln \rho(i) + \sum_{k=1}^{m_1} \cdot \ln\left(1 + \frac{\rho(k)}{k-i}\right)$$

But since, $0 < \rho(k) < 1$, the above can be expanded in a Taylor series, and it is found that, as $m_1 \to \infty$

$$B(p) =$$
$$\rho(p) \exp\left\{P \int_l^h \frac{\rho(\lambda)}{\lambda - p} d\lambda - \sum_1^\infty \frac{[\rho(p)]^{2i}}{i} Z(2i)\right\} \quad (7.7)$$

for $l \leq p < h$, and where $Z(2i)$ is the Riemann zeta function. Similarly it can be shown that (6.19a) becomes

$$B(p) = \exp\left(\int_l^h \frac{\rho(\lambda)}{\lambda - p} d\lambda\right)$$

for $p < l$. It is worth pointing out that (7.7) is the solution to the integral equation

$$P \int_l^h \frac{B(p)}{\lambda - p} dp + B(\lambda)\,\pi \cot \pi \rho(\lambda) = 1 \quad (7.8)$$

$l \leq \lambda < h$, where $\rho(\lambda)$, $0 < \rho(\lambda) < 1$, is a known function. It can be shown that as $p \to l$

$$B(p) \to K \left(\frac{1}{p-l}\right)^{\rho(l)}$$

and therefore $B(p)$ is integrable.

Finally, the limiting form of (6.20) becomes

$$p\,D\,x_0(p) = B(p)\left\{RD + \int_0^l \frac{q\,x_p(q)}{B(q)\,(q-p)} dq\right\} \quad (7.9)$$

for $l \leq p < h$, while

$$RD = \int_0^l \frac{q\,x_p(q)}{B(q)\,(l-q)} dq \qquad (7.9a)$$

since $B(l)$ is infinite, and

$$D = \int_0^h D\,x_0(p)\,dp \qquad (7.9b)$$

It is again interesting to point out that (7.9) is the solution to the integral equation

$$P \int_l^h \frac{p\,D\,x_0(p)}{\lambda - p} dp + \lambda\,D\,x_0(\lambda)\,\pi \cot \pi \rho(\lambda)$$
$$= RD - \int_0^l \frac{p x_p(p)}{\lambda - p} dp$$

for $l \leq \lambda < h$.

Thus far it has been assumed that $x_p(p)$ did not vanish along the p axis. Let it be supposed now that $x_p(p)$, $l \leq p \leq h$, vanishes only and everywhere in the set of intervals B, $b_k < p < a_k$, $k = 1, 2, \ldots c$, where $a_1 > a_2 \ldots > a_c$ and let the remaining part of the interval $l \leq p \leq h$ be A.

Now the limiting form of (6.18) is given by

(7.6) for λ in A, but, in addition, c numbers λ_k, λ_k in B, can be found such that

$$\int_0^\infty \frac{p\,x_F(p)}{\lambda_k - p}\,dp = -q \qquad (7.10)$$

It follows then that the limiting forms of (6.19) and (6.19a) are respectively

$$B(p) = \frac{\overset{c}{\underset{1}{\pi}}(\lambda_k - p)}{\overset{c}{\underset{1}{\pi}}(b_k - p)} \exp$$

$$\left\{ P\int_l^h \frac{\rho(\lambda)}{\lambda - p}\,d\lambda - \sum_1^\infty \frac{[\rho(p)]^{2i}}{i}\,Z(2i) \right\} \quad (7.11)$$

for all p in A, and

$$B(p) = \frac{\overset{c}{\underset{1}{\pi}}(\lambda_k - p)}{\overset{c}{\underset{1}{\pi}}(b_k - p)} \exp \int_l^h \frac{\rho(\lambda)}{\lambda - p}\,d\lambda \quad (7.11a)$$

for $p < l$. With these new definitions Eqs. (7.9), (7.9a) and (7.9b) remain unchanged.

It must be kept in mind, however, that the two points h and l are, in general, not specified *a priori*. But, at any rate, it is best to assume h and l first and then to solve (7.9) and (7.9a). This process should be repeated, until the calculated values for $x_0(p)$ at the two points $p = \beta$ and $p = \beta^*$ coincide with those stated in the problem.

2. *Semi-continuous mixtures.* By definition the distribution function of a semi-continuous mixture is everywhere single valued and continuous except at a finite number of points where it possesses infinite but integrable discontinuities. In section 4 of the previous paper, the fractionation of semi-continuous mixtures in an ideal cascade were considered. The minimum reflux problem for semi-continuous mixtures will not be worked out here except to say that the problem can be solved without much difficulty in the manner shown in the previous part of the present paper. It should be pointed out, however, that for every integrable infinite discontinuity in $x_F(p)$, for $l < p < h$, there

is an integrable infinite discontinuity in $B(p)$ – defined by a proper generalization of (7.11) – at precisely the same values of p.

8. CONCLUSIONS

The minimum reflux problem in the rectification of multi-component and complex mixtures in an ideal cascade has been solved exactly. By means then of the formulae presented in this paper it is possible to calculate, not only the minimum reflux, for a specified separation, but also the composition of the product streams.

One of the main characteristics of this problem is the appearance of the two points h and l which are unambiguously defined. The value of both h and l will depend, of course, not only on the composition and the thermal condition of the feed, but also on the desired separation, which is specified by giving the value of $x_0(p)$ at two points, say $p = \beta$ and $p = \beta^*$. In any actual calculations it is however preferable to assume h and l, until the calculated values of β and β^* coincide with those given.

In addition, the form of (7.3) and the analogous expression for the stripping column correctly predict that, in general, the cascade can be broken up, at minimum reflux, into five sections. The two sections, the so-called " pinches," which contain the infinite number of plates are, respectively, above and below the section containing the feed plate. Moreover, the composition of the various streams does not change, from plate to plate, in the two pinched reagions, whereas it does change in the other three sections. It can easily be shown from (7.3) that, in the pinched region of the enriching section,

$$x_n'(p) = \frac{p\,x_0(p)}{R(h - p)}$$

for $p < h$, while $x_n(p) = 0$ for $p > h$. Similarly, in the pinched region of the stripping section,

$$x_s^\bullet(p) = \frac{p\,x_0^*(p)}{R^*(p - l)}$$

for $p > l$, while $x_s^*(p) = 0$ for $p < l$. The above relations hold for all mixtures.

NOTATION

A_k = function defined by Eq. (6.16)
$B(k)$ = function defined by Eq. (6.17)
C_k = function defined by Eq. (3.11)
C_k^* = function corresponding to C_k for stripping section
G_k = function defined by Eq. (6.2)
G_k^* = function defined by Eq. (6.3)
h, l = key components
N = number of plates in rectification section
$p(i)$ = reciprocal relative volatility of ith component
q = thermal factor for column feed
R = rectification section reflux ratio
R^* = stripping section reflux ratio
r_j = function defined by Eq. (6.7a)
r_j^* = function defined by Eq. (6.7b)
S = number of plates in stripping section
$x_0(i)$ = overhead composition function
$x_0^*(i)$ = residue composition function
Z = function defined by Eq. (6.4)
ϕ_k = characteristic root for stripping section
λ_k = characteristic root for rectification section
$\rho(\lambda)$ = function defined by Eq. (4.15)
$\zeta(z)$ = Riemann zeta function

Other symbols defined in Part I.

REFERENCES

[1] UNDERWOOD, A. J. V.; *Chem. Eng. Prog.* 1948 **44** 603.

[2] MURDOCH, P. G. and HOLLAND, C. D.; *Chem. Eng. Prog.* 1952 **48** 287.

[3] ACRIVOS, A.; Ph.D. Thesis, University of Minnesota, 1954.

Thermodynamic evaluation of binary vapour-liquid equilibria

H. A. C. THIJSSEN

Laboratory of Physics and Meteorology, Agricultural University, Wageningen, The Netherlands.

Summary—An exact graphical method for the evaluation of vapour-liquid equilibrium data in a binary mixture from boiling point composition data is described. The variation of the activity coefficients with composition is obtained by successive application of the exact Duhem equation to a graph relating $\ln \gamma_1$, and $\ln \gamma_2$ with x as parameter. Further, the test for internal consistency of vapour-liquid equilibrium data as introduced by HARINGTON is extended to p constant, T variable and corrected for nonideality of the vapour phase. The methods are applied to vapour-liquid equilibrium data of the binary system methylcyclohexane-toluene.

Résumé—L'auteur décrit une méthode graphique exacte pour vérifier à partir de la courbe d'ébullition d'un mélange binaire, les données de l'équilibre liquide-vapeur. Il obtient la variation des coefficients d'activité avec la composition par application de la forme exacte de l'équation de DUHEM à un graphique reliant $\ln \gamma_1$ et $\ln \gamma_2$ avec x comme paramètre.

En outres, il étend le test introduit par HARINGTON qui apprécie la qualité intrinsèque des données de l'équilibre liquide vapeur, à p constant et T variable et le corrige dans le cas de non idéalité de la phase vapeur. Il applique cette méthode aux données de l'équilibre liquide-vapeur du système binaire methyl-cyclohexane – toluène.

THE GIBBS-DUHEM EQUATION

The general form of the Gibbs-Duhem equation for binary mixtures valid at variable T and p is

$$n_1 \, d\mu_1 + n_2 \, d\mu_2 = V dp - S dt \qquad (1)$$

If we replace the chemical potentials μ by the fugacity according to the definition of the fugacity

$$d\mu_1 = RT \, d \ln f_1 \quad \text{at } T \text{ constant}$$

and divide by the sum of the mole numbers, eq. (1) takes the form

$$x_1 \, d \ln f_1 + x_2 \, d \ln f_2 = 0 \text{ at } T \text{ and } p \text{ constant} \qquad (2)$$

Introducing the partial derivatives of $\ln f$ with respect to the mole fraction of one of the components, eq. (2) reduces to the common Duhem equation :

$$x_1 \left(\frac{\partial \ln f_1}{\partial x_1} \right)_{T, p} = x_2 \left(\frac{\partial \ln f_2}{\partial x_2} \right)_{T, p} \text{ or, since } \gamma_1 = \frac{f_1}{x_1 f_1^\circ}$$

$$\left(\frac{\partial \ln \gamma_1}{\partial \ln x_1} \right)_{T, p} = \left(\frac{\partial \ln \gamma_2}{\partial \ln x_2} \right)_{T, p} \qquad (3)$$

In case of a two phase-system, eq. (3) is not valid as equilibrium relation, since according to the phase rule it is impossible to maintain equilibrium if the composition is varied at constant temperature and pressure.

BARNETT F. DODGE [2] showed by a comparative study of the convential Gibbs-Duhem equation and his derivation of the exact relationship valid at p constant and T variable that even for rather close-boiling mixtures the degree of inaccuracy in the extremes of the concentration range may amount to 10% or more.

The advantage of integrated approximation forms of eq. (3) as developed by VAN LAAR, MARGULES, SCATCHARD and others is that only two experimental constants, e.g. A_1 and A_2 are involved [1, 5, 9]. From a number of experimental vapour-liquid data an average A_1 and A_2 can thus be determined, and assuming eq. (3) to be valid, an accurate calculation of the equilibrium curve can be made.

Theoretically, one single equilibrium measurement in a binary mixture including a determination of the temperature is sufficient to calculate the two constants, from which the whole equilibrium curve can be calculated.

An excellent review and critical study of the equations mentioned is given by WOHL [11].

Apart from the limited validity of such a calculation owing to the assumption that T and p are constant, the equal influence of the vapour-liquid compositions and of the temperature on the accuracy of the activity coefficient must be seen as a drawback. Thus, a possible error in the analysis or a departure from equilibrium will be enhanced by errors in the temperature. It is concluded, therefore, that a testing method insensible to errors in the temperature or a direct calculation from boiling point-composition data is to be preferred.

EVALUATION OF VAPOUR-LIQUID EQUILIBRIUM CURVES FROM BOILING POINT-COMPOSITION DATA

CARLSON and COLBURN [1] suggested a procedure utilizing the relations

$$\gamma_1 = \frac{p - \gamma_2 P_2 x_2}{P_1 x_1} \quad \text{and} \quad \gamma_2 = \frac{p - \gamma_1 P_1 x_1}{P_2 x_2}, \quad (4)$$

For a given T, x diagram γ_1 can be calculated as a function of the liquid composition if to a first approximation it is assumed that $\gamma_2 = 1$, and also γ_2 can be calculated assuming $\gamma_1 = 1$. By plotting these apparent activity coefficients against composition the terminal values of γ_1 and γ_2 can be obtained by extrapolation which logarithms are the constants in the van Laar or Margules equations.

OTHMER, RICCIARDI and THAKAR [4] converted the Gibbs-Duhem equation at constant T and p to an equation representing x, y, T at constant pressure from which the vapour composition could be obtained by stepwise integration.

A similar relationship was derived by REDLICH and KISTER [8], it involved however an assumption whereby the variation of the activity coefficients with temperature at constant composition was assumed to be negligible.

Although the method of OTHMER is thermodynamically exact except for the assumed ideality of the vapour-phase the procedure of CARLSON and COLBURN is still to be preferred as this method offers a possibility for corrections of experimental errors. With OTHMER's method,

the equilibrium curve becomes, particularly in the low and high concentration range, extremely sensitive for errors in the T, x diagram.

An exact method will now be derived with retention of the possibility for correction of incidental errors in the T, x diagram while thermodynamical inconsistencies can be easily detected.

The variation of the activity coefficients with temperature at constant composition and pressure can be related to the relative partial molal enthalpy according to

$$\frac{d \ln \gamma_1}{d T} = -\frac{\Delta L_1}{R T^2} \quad (5)$$

where ΔL_1, is the partial molal enthalpy of component 1 in solution minus the enthalpy of the pure component at the same temperature.

As $\Delta L = \Delta L_1 x_1 + \Delta L_2 x_2$, where ΔL is the integral heat of mixing per mole of mixture, the following relation between the activity coefficients of component 1 and 2 can be derived.

$$x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2 = -\frac{\Delta L}{R T^2} d T \text{ (at } p \text{ constant)} \quad (6)$$

By writing eq. (9) as partial derivatives with respect to the mole fraction of component 1, a modified Duhem equation valid at p constant and T variable is obtained.

$$x_1 \frac{\partial \ln \gamma_1}{\partial x_1} = x_2 \frac{\partial \ln \gamma_2}{\partial x_2} - \frac{\Delta L}{R T^2} \frac{\partial T}{d x_1} \quad (7)$$

or

$$\Delta \ln \gamma_2 = -\frac{x_1}{1 - x_1} \Delta \ln \gamma_1 - \frac{1}{1 - x_1} \frac{\Delta L}{R T^2} \Delta T \quad (7a)$$

The relationship between γ_1 and γ_2 can be written as

$$\gamma_1 = \frac{p}{x P_1 v_1} - \frac{1 - x}{x} \frac{P_2}{P_1} \frac{v_1}{v_2} \gamma_2 \quad (8)$$

in which $v = \exp -\frac{(V_1 - B_1)(P_1 - p)}{R T}$, the correction term for the non ideality of the vapour phase [6, 10].

For a given T, x diagram γ_1, can now be

calculated for $\gamma_2 = 1$ as a function of the liquid composition and also γ_2 for $\gamma_1 = 1$. As an example, the binary system methylcyclohexane-toluene is given in Fig. 1. The T, x data of QUIGGLE and FENSKE [7] are used for this purpose. As the curvature of the calculated curve is very small, extrapolation to the high and low concentration ranges where the data points show
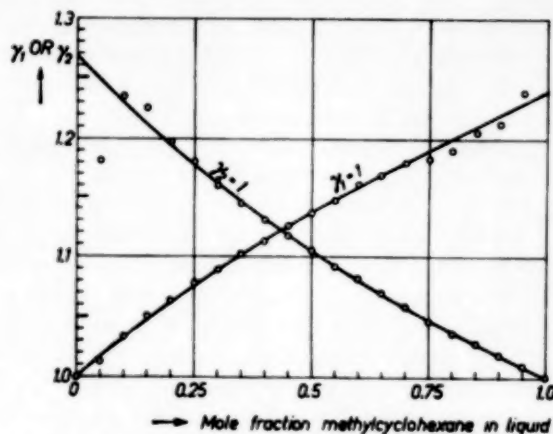
FIG. 1. Plot of γ_1, and γ_2 vs. liquid composition for $\gamma_2 = 1$ and $\gamma_1 = 1$ respectively.

a large scattering is easily possible. The deviations in these ranges are caused by inaccuracies in the determination of the T, x diagram or departure from equilibrium.

According to eq. (3) $\dfrac{d^2 \gamma_1}{dx_1{}^2} \cdot \dfrac{d x_2{}^2}{d^2 \gamma_2}$ is 0 and ∞ for $x = 0$ and $x = 1$ respectively; thus the intersections of the two curves in Fig. 1 with the
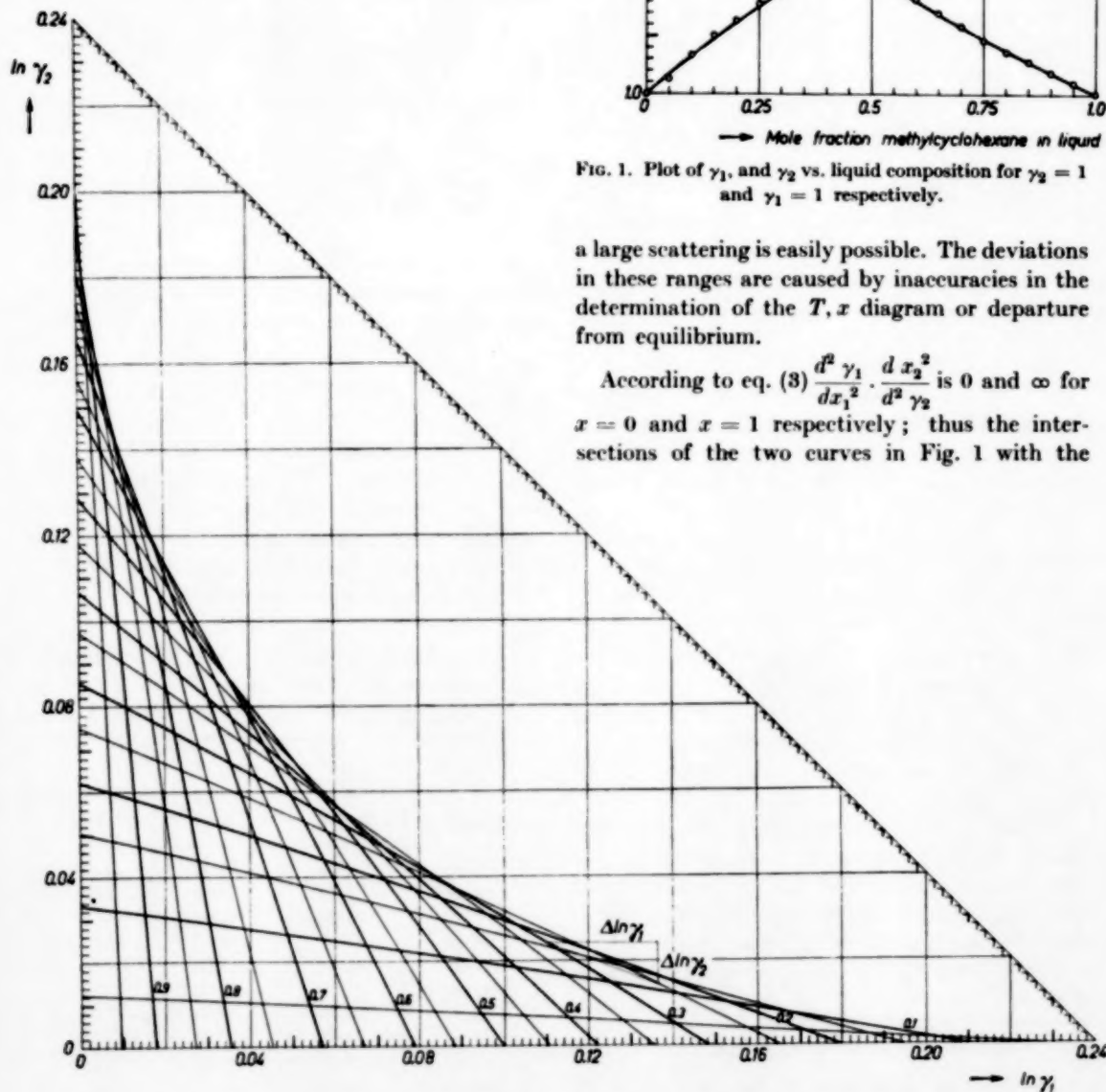
FIG. 2. Relation between ln γ_1 and ln γ_2 with liquid composition as parameter.

77

ordinates at $x = 0$ and $x = 1$ represent the maximum endvalues of the activity coefficients.

In Fig. 2 the logarithms of the smoothed pseudo-activity coefficients are used for the graphical representation of eq. (8), the parameters are taken as $x = 0.05 - 0.10 \ldots 0.95$.

It is clear that by stepping over from curve $m \, \Delta x$ to curve $(m + 1) \, \Delta x$ the accompanying change of $\Delta \ln \gamma_1$, and $\Delta \ln \gamma_2$ must satisfy eq. (7a.)

From the T, x data and starting with the value of $\ln \gamma_1$, for $x = 0$ and $\ln \gamma_2 = 0$ obtained from the graphical extrapolation in Fig. 1 it is now possible, by applying equation (7a) to Fig. 2, to draw the entire curve of the activity coefficients with composition.

A simple procedure is to plot the $\ln \gamma_1$, $\ln \gamma_2^{\bullet}$ relation on transparent paper, using a graph of eq. (7a) with $0.5 \, \Delta x - 1.5 \, \Delta x \ldots (1 - 0.5 \, \Delta x)$, as parameter at the same scale, which is put under the transparent paper, and then to step off the successive curves starting with γ_1 for $x = 0$.

The graphically extrapolated endvalues of γ_1 and γ_2 in Fig. 1 should strictly satisfy the new values obtained by eq. (7a) and (8), consequently thermodynamic inconsistencies in the boiling point - composition diagram can be easily detected.

An Exact Test for the Internal Consistency of Vapour-Liquid Equilibria Data

It is noted by several authors [3, 8] that the relation between F^E denoting the excess free energy of formation of a mixture over an ideal mixture of the same composition, and the relative volatility α is eminently suited for testing vapour-liquid equilibria.

However, the authors cited, assumed the simple form of the Duhem equation [3] to be valid and did not correct for the non ideality of the vapour phase. An analogous relation that is free of these limitations will now be derived.

From the definition of the excess free energy it follows

$$F^E = RT \, (n_1 \ln \gamma_1 + n_2 \ln \gamma_2) \qquad (9)$$

By dividing expression (9) by the sum of the number of moles and differentiating with respect

to the obtained mole fraction it takes the form

$$\frac{dF^E}{dx_1} = x_1 \frac{d \ln \gamma_1}{dx_1} - x_2 \frac{d \ln \gamma_2}{dx_2} + \ln \frac{\gamma_1}{\gamma_2} \qquad (10)$$

Introducing the Gibbs-Duhem equation valid at p constant

$$x_1 \frac{d \ln \gamma_1}{dx_1} - x_2 \frac{d \ln \gamma_2}{dx_2} = - \frac{\Delta L}{RT^2} \cdot \frac{dT}{dx}$$

we see that

$$\frac{dF^E}{dx} = - \frac{\Delta L}{RT^2} \cdot \frac{dT}{dx} + \ln \frac{\gamma_1}{\gamma_2}$$

After integration between the limits $x = 0$ and $x = 1$

$$\int_0^1 \left(- \frac{\Delta L}{RT^2} \cdot \frac{dT}{dx} \right) dx + \int_0^1 \ln \frac{\gamma_1}{\gamma_2} \, dx = 0 \qquad (10a)$$

By combination of eq. (10a) and the relationship for vapour liquid equilibria corrected for the nonideality of the vapour phase [6] it follows that:

$$\int_0^1 \left(- \frac{\Delta L}{RT^2} \cdot \frac{dT}{dx} \right) dx + \int_0^1 \left(\ln \alpha - \ln \frac{P_1 v_1}{P_1 v_2} \right) dx = 0 \qquad (11)$$

An application of this equation to the calculation of ΔF^E from the vapour-liquid equilibria data of the system methylcyclohexane-toluene, as determined by QUIGGLE and FENSKE and The Central Institute for Physico Chemical Constants, Utrecht, Table 1 is illustrated in Fig. 3.

Table 1. *Vapour-liquid equilibria in methylcyclohexane-toluene at 760 mm Hg. Central Institute for Physico Chemical Constants, Utrecht.*

Mole % volatile component in :			
Liquid	Vapour	Liquid	Vapour
5.00	7.70	55.00	60.80
10.00	14.60	60.00	65.00
15.00	21.00	65.00	69.25
20.00	27.00	70.00	73.55
25.00	32.60	75.00	77.85
30.00	42.95	80.00	82.15
35.00	47.70	85.00	86.45
40.00	52.20	90.00	90.80
45.00	56.50	95.00	95.40
50.00	60.80		

DISCUSSION

In Fig. 3 $\ln \frac{\gamma_1}{\gamma_2}$, calculated according to the method of CARLSON and COLBURN in combination with MARGULES, is plotted along with dF^E/dx against the molal liquid composition. The dotted line represents the deviation term $\frac{\Delta L}{RT^2} \cdot \frac{dT}{dx}$ from the commonly applied Duhem equation. As mentioned before, eq. (3) may hold fairly well in a certain part of the diagram and still be in serious error at the extremes of the concentration range. At 0·025 mole fraction the value of $\frac{d \ln \gamma_1}{d \ln x_1}$ calculated from Fig. 2 and eq. (7a) is approximately 0·0125 and

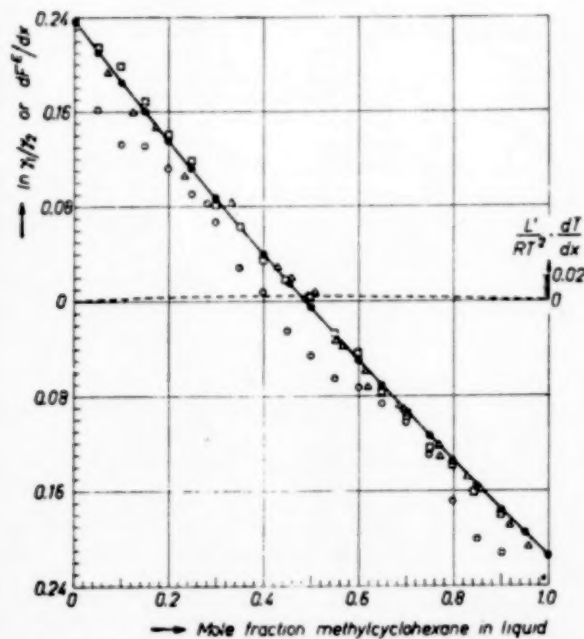$$\frac{\Delta L}{RT^2} \cdot \frac{dT}{dx} = 0.0007.$$

FIG. 3. Plot of $\ln \gamma_1/\gamma_2$ or dF^E/dx vs. molal liquid composition for methylcyclohexane-toluene.

$\ln \gamma_1/\gamma_2$ refers to the method of CARLSON and COLBURN only.

● method of CARLSON and COLBURN ⎫ T, x data of
▢ method of present author ⎬ QUIGGLE and
△ x, y data of the Central Institute. ⎭ FENXKE
○ x, y data of QUIGGLE and FENSKE.

Both sides of eq. (3) differ, therefore, by 5·6% when $x = 0.025$.

From a comparison of the areas bounded by the curve lying above the zero line and the $\frac{\Delta L}{RT^2} \cdot \frac{dT}{dx}$ curve it follows that by neglecting the latter term the overall error in eq. (3) is only 3%. The deviation of the logarithms of the end values calculated from the Margules equation is about 1·5%.

The T, x data of QUIGGLE and FENSKE appear to be consistent, thermodynamically, and agree excellently with the vapour-liquid equilibrium data of the Central Institute for Physico Chemical Constants. The x, y data of QUIGGLE and FENSKE, however, are at variance with any equilibrium relation.

It is interesting to note that, on the contrary, these authors strongly stressed that conclusions as to the validity of equilibrium data should not be drawn from temperature, composition data as the accuracy of analysis by density or refractive index is much higher than those of temperature measurements.

NOTATION

A_1, A_2 = constants in the Margules equation.

B = virial coefficient.

F^E = excess free energy.

f = fugacity.

ΔL = integral heat of mixing per mole of mixture.

ΔL_1 = partial molal enthalpy of component in solution minus the enthalpy of the pure component at the same temperature.

n = number of moles.

P = vapour pressure of pure component.

p = total pressure.

R = gas constant.

T = absolute temperature.

V = molal volume of component in liquid at temperature of system.

v = correction term for the nonideality of the vapour phase.

x = mole fraction of volatile component in liquid.

y = mole fraction of volatile component in vapour.

γ = activity coefficient.

μ = chemical potential of a component.

Subscripts 1 and 2 signify volatile and less volatile component respectively, l and g are abbreviations for liquid - and vapour phase.

REFERENCES

[1] CARLSON, H. C. and COLBURN, A. P.; *Ind. Eng. Chem.* 1942 **34** 581.

[2] DODGE, BARNETT, F.; *Chem. Eng. Sci.* 1953 **2** 120.

[3] HERINGTON, E. F. G.; *Nature* 1947 **160** 610.

[4] OTHMER, D. F., RICCIARDI, L. G. and THAKAR, M. S.; *Ind. Eng. Chem.* 1953 **45** 1815.

[5] PERRY, J. H.; *Chemical Engineer's Handbook* 1950, p. 527.

[6] PERRY, J. H.; *Chemical Engineer's Handbook*, 1950, p. 537.

[7] QUIGGLE, D. and FENSKE, M. R.; *J. Amer. Chem. Soc.* 1937 **59** 1829.

[8] REDLICH, O. and KISTER, A. T.; *Ind. Eng. Chem.* 1948 **40** 341.

[9] SCATCHARD, G. and HAMER, W. J.; *J. Amer. Chem. Soc.* 1935 **57** 1805.

[10] WOHL, K.; *Z. phys. Chem.* 1929 **B2** 77.

[11] WOHL, K.; *Trans. Amer. Inst. Chem. Engrs.* 1946 **42** 215.

Distillation column for study of individual plate efficiencies

H. A. C. Thijssen

Laboratory of Physics and Meteorology, Agricultural University, Wageningen, The Netherlands

Summary—A laboratory sieve plate column is described for studying the influence of type of mixture and operating variables on plate efficiencies. Special care has been given to the possibility of regulating and measuring flow of matter and heat to individual trays.

Résumé—L'auteur décrit une colonne de laboratoire à plateaux perforés pour étudier l'influence du type de mélange et travailler avec des efficacités variables sur les plateaux. Il a soigné particulièrement la possibilité de régler et de mesurer les alimentations et les apports thermiques sur les plateaux individuels.

Introduction

A considerable number of methods for predicting plate efficiencies in distillation columns has been proposed [1, 2, 3, 4, 5]. Many of these are correlation methods, based upon empirical relationships, others have a theoretical foundation. It is, however, necessary to introduce experimental factors in the latter cases as well, owing to the complexity of the phenomena of mass and heat transfer at the conditions prevailing in distillation columns.

Unless a more fundamental understanding of these phenomena becomes available a large number of experiments continue to be necessary if other types of trays are considered, e.g., with respect to excessive fouling as may occur with some agricultural products, or if mixtures are separated which possess properties largely different from those of the mixtures commonly used.

With the object to obtain data of a fundamental character, a laboratory column has been constructed with which the efficiency of individual plates can be studied. Special care has been given to the possibility of regulating and measuring flow of matter and heat for individual plates. Instead of using a few trays only as is often done in tray efficiency studies, a larger number was deliberately installed to enable a comparison of conditions for mixtures of different types under nearly the same conditions. In the present paper the column is described in detail together with an example of the results obtained. Complete results have been discussed in a previous paper [6].

Tray and Column Design

The column is composed of 5 measuring and 4 glass sections in alternate position. Each section except the uppermost contains a sieve plate. All necessary data, viz. liquid flowrate, temperature, composition and heat transfer through the wall, can be obtained from a measuring section.

The condenser and reflux divider are mounted directly over the top section. The measuring sections are insulated by 1 cm of glass blanket, the glass sections by means of a double wall. Every section is surrounded by a jacket constructed partly of glass, the temperature of which can be regulated by means of a set of heating coils. Temperature control to within $\pm 1°C$ can be achieved. In order to enable a study of different types of sieve plates, it was necessary to have a free plate surface with a minimum of 2 rows of holes at a pitch of 15 mm. The limitations imposed with regard to the minimum downcomer and liquid seal dimensions dictated a minimum column diameter of 38 mm. For the present series of runs the hole diameter was held constant at 0·75 mm on a 3·0 mm pitch. The design of a measuring section is shown in Fig. 1. Table 1 summarizes the dimensions of a sieve plate.

For the measurements of the liquid rates on the trays a new type of siphon-flowmeter was developed which combines small dimensions (7 cm) and a measuring range of 0·01-1 cc/sec with an accuracy of about 3%.

Table 1. Summary of plate dimensions.

Inside diameter of column, cm	3·8
Plate spacing, cm	12·0
Holes/plate	97
Hole diameter, cm	0·075
Drilling pattern	Equilaterial triangular
Distance between hole centres, cm	0·3
Weir height, cm	1·0
Inside diameter of downpipe, cm	1·0

At closed position of valve V_1 the liquid flows via downpipe D_1 in the siphon which will fill to A and empty. The period of siphoning T comprises the time required to fill the siphon at a flowrate of Q cc/sec and a time t' required for emptying; hence $T = b/Q + t'$, where b is the effective volume of the siphon. A ciné-camera served for the measurement of t'.

The pulsating effect of the siphon on the reflux is eliminated to some extent by means of buffer tank T. Valve V_2 can be so adjusted that for a siphon content of 4 cc and the dimensions given in Fig. 1 the ripple is limited to 8%. These fluctuations do not interfere with the operation of the column since the siphons are only in the circuit during flow measurements. Normally, the liquid downflow runs via the downpipe straight to the next tray. Even when measuring flowrates
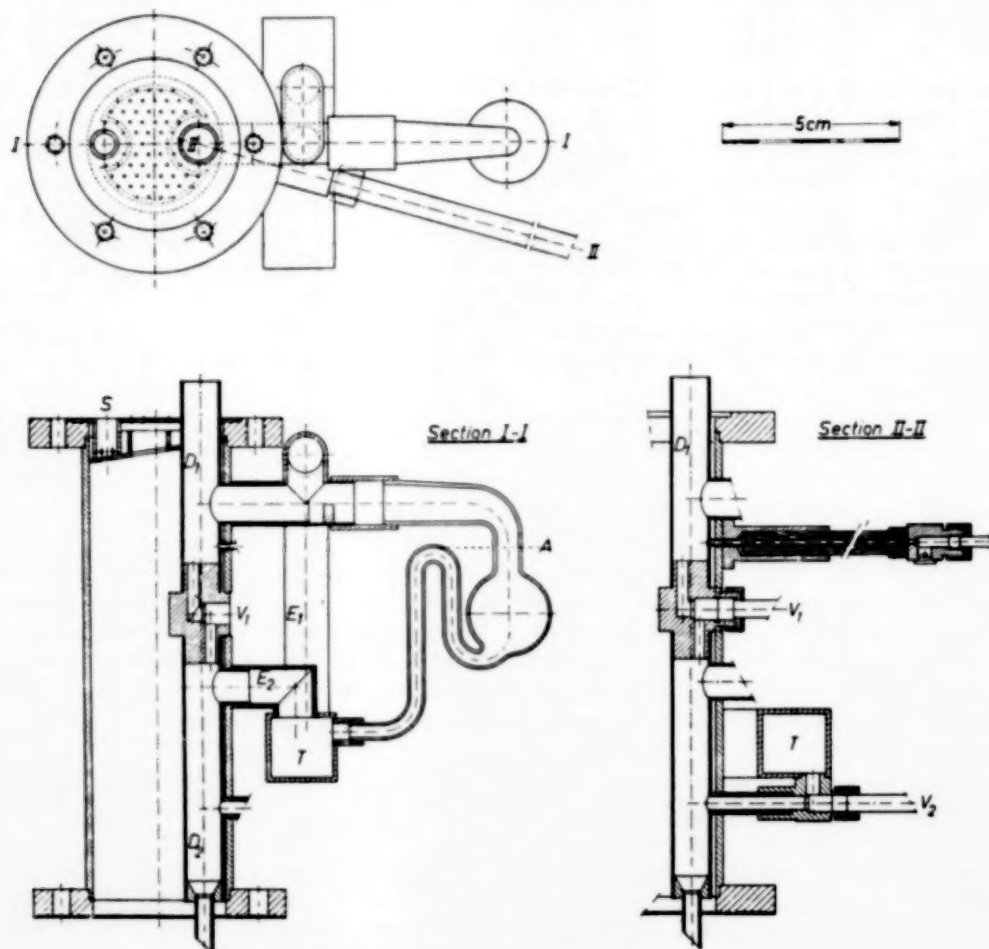

FIG. 1. Measuring section of sieve plate column.

82

the disturbances are only local since only one siphon is used at a time.

Pipe E_1 serves for exhausting the buffer-tank. Emptying the siphon has to be accompanied by the rapid removal of 4 cc of gas from T, as otherwise an overpressure relative to the siphon inlet would develop in the buffer-tank which would prevent siphoning. Large values of the equilibrium constants, resulting in big temperature differences between successive plates, may cause flashing of the liquid and, in consequence, a vapour lift in the downpipe D_2. This is prevented by the exhaust pipe E_2 so the flashed liquid circulates only in the circuit formed by E_2 and T, in which T serves as a liquid separator.

The large diameter of the exhaust pipe is required to prevent the formation of liquid droplets in it which would hinder rapid exhausting and, in consequence, the proper action of the siphon. In order to avoid too large holdups, the distance between buffer-tank and sieve plate is chosen so that at normal throughputs the tank drains entirely. It appeared from the temperatures recorded that flow-measurements do not influence the plate efficiency.

The results of the flowmeter measurement are, naturally, only reproducible by working above the so-called " weep-point " of the sieve trays. In order to make possible measurements below the weep-point, anti-weeptrays were constructed. Their action is based on the principle that the pressure in the section below the tray under consideration is greater than the pressure at the bottom of liquid seal S, so leaking liquid will be driven back through the drainage holes via the liquid seal to the tray. Since the liquid runs as a film along the surface of the tray to the edge and there drips off, a narrow annular model as shown in the figure was sufficient.

Sample taps specially designed for withdrawal of small samples (0·2 to 0·4 cc) are provided on all measuring sections and on two of the glass ones. The vapour sample inlet of section 6 is located about 0·5 cm below the anti-weep tray and exactly in the centre of it. The liquid remaining in the sample line is blown back into the column just before sampling.

Every section is provided with a thermo-

element. The temperatures of the vapour as well as the temperature differences between the section and its heating jacket were measured by means of a specially designed circuit. In order to avoid
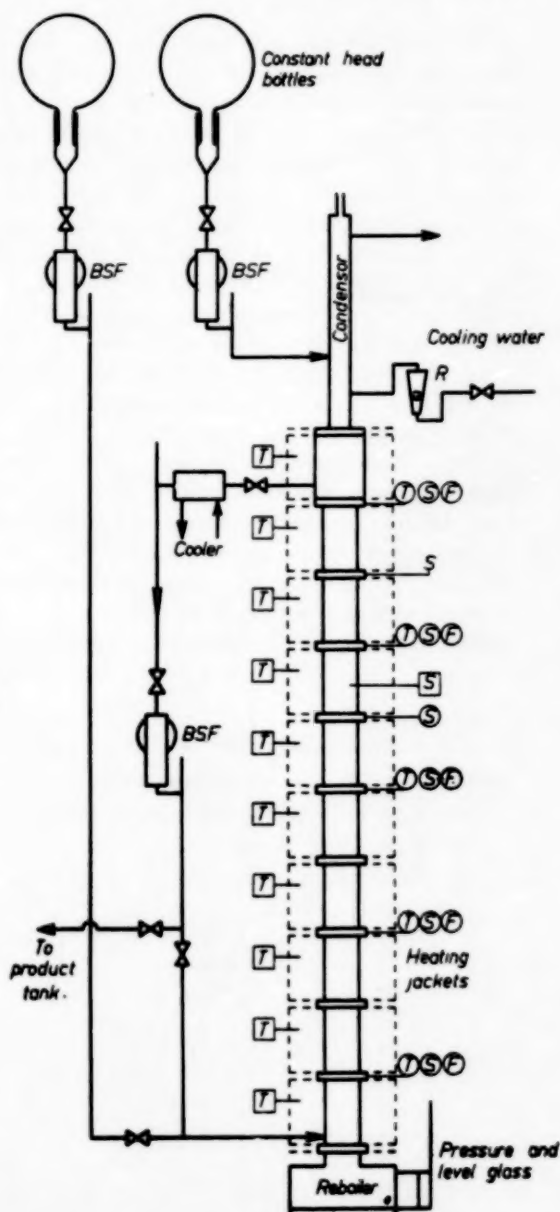

FIG. 2. Flow sheet of laboratory distillation unit. B $S.F.$ – buffered siphon flowmeter; F – flowmeter; S – sample tap; T – thermocouple; R – rotameter.

an intermittent distillation caused by boiling retardation and non-mixing in the reboiler, a mixer was installed in it.

FLOW SHEET

A flow sheet for the operations is given in Fig. 2. Overhead vapour is wholly condensed. For runs under finite reflux a part flows by gravity via pilot valve and flowmeter to the reboiler. For runs with total reflux for one component only the distillate is removed as product. Total reflux for one component only is achieved by supplying one pure component from a constant head tank via the measuring and regulating system to the reboiler, the other component from a similar system to the middle of the condenser, in order to avoid upsetting of the heat balance and the plate efficiency, and removing as much distillate as amounts to the total supply of pure components. The upper section does not contain a sieve plate and the reflux from the condenser flows directly through downpipe or siphonmeter. The supply of pure components and removal of distillate is controlled by means of completely buffered siphon-flowmeters. The flowrate of cooling water in the condenser is controlled with

the aid of a rotameter. A continuous record of the vapour temperatures of all sections is obtained by means of a 12-point recorder.

A run at total reflux of the volatile component only is illustrated in Fig. 3.
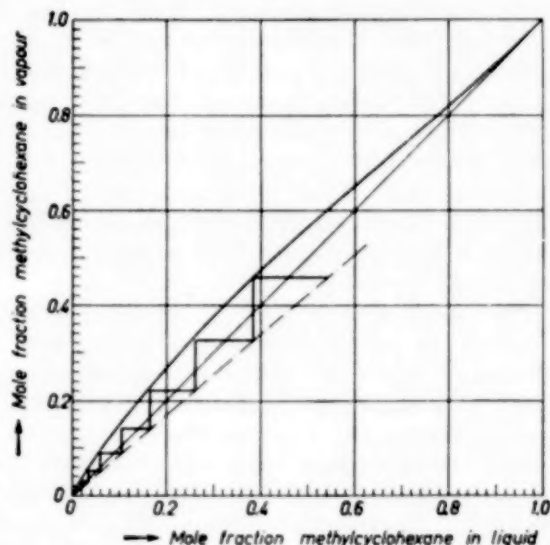
FIG. 3. McCabe-Thiele diagram of methylcyclohexane-toluene at partial reflux of the volatile comp. only, $L/V = 0.84$.

REFERENCES

[1] GEDDES, R. L.; *Amer. Inst. Chem. Engrs.* 1946 **42** 79.

[2] WALTER, J. F. and SHERWOOD, T. K.; *Ind. Eng. Chem.* 1941 **33** 493.

[3] GERSTER, J. R., COLBURN, A. P., BONNET, W. E. and CARMODY, T. W.; *Ind. Eng. Chem.* 1949 **45** 716.

[4] WEST, F. B., GILBERT, W. D. and SHIMIZU, T.; *Ind. Eng. Chem.* 1952 **44** 2470.

[5] BAKOWSKI, S.; *Chem. Eng. Sci.* 1952 **1** 266.

[6] VAN WIJK, W. R. and THIJSSEN, H. A. C.; *Chem. Eng. Sci.* 1954 **3** 153.

Rectification of multicomponent mixtures

A. M. ESHAYA

The Coca-Cola Export Corporation, 515 Madison Avenue, New York, N.Y.

Summary—On the assumption that the relative volatilities, α, and the molal overflow are constant in a given column section, a comparatively simple and rapid method of performing multicomponent fractionation calculations is developed. The proposed method enables one to calculate by means of tabulated values of the functions E_1 and E_2 directly the composition on the nth plate without going through calculations of the compositions on the intermediate plates. This is done by means of the simple equations :

$$x_n = x_f\, E_1 + \frac{x_d\,(p_r - 1)}{p_r}\, E_2 \text{ (in rectifying section)}$$

$$x_m = x_w\, E_1 + \frac{x_w\,(p_s - 1)}{p_s}\, E_2 \text{ (in stripping section)}$$

E_1 and E_2 are functions of the equilibrium ratio, reflux ratio, and the number of the plate. Their values may be obtained from suitable tables or plots.

It is believed that the proposed method offers considerable simplification in multicomponent rectification calculations. The final equations are tested and their use demonstrated in two examples.

Résumé—En supposant que les volatilités relatives, α, et le flux moléculaire sont constants dans une section donnée de la colonne, l'auteur expose une méthode comparativement simple et rapide pour effectuer les calculs dans la séparation fractionnée d'un mélange à plusieurs composants. La méthode proposée permet, à partir de tables des valeurs des fonctions E_1 et E_2, de calculer directement la composition sur le nième plateau sans passer par le calcul des compositions sur les plateaux intermédiaires. Ce qui se fait par les équations simples :

$$x_n = x_f\, E_1 + \frac{x_d\,(p_r - 1)}{p_r}\, E_2 \text{ (in rectifying section)}$$

$$x_m = x_w\, E_1 + \frac{x_w\,(p_s - 1)}{p_s}\, E_2 \text{ (in stripping section)}$$

E_1 et E_2 sont des fonctions du taux d'équilibre du reflux et du nombre de plateaux. Leurs valeurs peuvent être obtenues à partir de tables ou de courbes appropriées.

L'auteur pense que la méthode proposée présente une simplification considérable dans les calculs de la rectification de mélanges à plusieurs composants. Il essaie les équations finales et démontre leur utilisation dans deux exemples.

The classical method of solving multicomponent rectification problems is that of LEWIS and MATHESON [3]. This method consists of plate-by-plate calculations starting with the still pot and continuing up the column until a composition approaching that of the feed is obtained. In a similar way, starting with the composition of the distillate, one proceeds down the column until a composition close to that of the feed is reached. Readjustment of the reflux ratio or of one of the starting compositions (waste or distillate) may be required to make the compositions " mesh " on the feed plate. This method (as well as its graphical equivalent, the method of LEWIS and COPE [2]) has the advantage that it may be carried to any degree of accuracy and may be easily combined

with enthalpy balances in the cases in which the assumption of equal molal overflow is not justified. The only disadvantage of these classical methods is the tediousness of the calculations involved : a trial and error procedure in the calculation of the composition of the vapour rising from each plate.

Because of the practical importance of the problem numerous workers in the field have proposed methods which are intended either to simplify the necessary calculations, or to give an answer to some specific aspect of the general problem. Important recent contributions have been that of MURDOCH and co-workers [4, 5, 6] who have presented a mathematical analysis of the general problem, and that of UNDERWOOD [8, 9, 10, 11, 12] who has developed a rigorous solution for the composition on the nth plate without going through plate-by-plate calculations for all intermediary plates. The method involves the solution of a system of equations, each system having as many equations and rootes as the number of components involved. The amount of numerical calculations required is thus considerable (see ref. 8).

The present method allows the calculation of the composition of the nth plate directly in a convenient way by means of tabulated functions.

One must consider first the following simplified problem :

A mixture of z components enters the feed plate and the composition of the mixture is known to be $x_{af}, x_{bf}, \ldots x_{zf}$. (Note : the first subscript refers to the component and runs from a to z; the second subscript refers to the number of the plate). The composition of the distillate is $x_{ad}, x_{bd}, \ldots x_{zd}$ and the composition of the waste is $x_{aw}, x_{bw} \ldots x_{zw}$. The reflux ratio is $R > R_{min}$, i.e. there are no " pinched in " regions in the section. The problem is to evaluate analytically the number of plates in the rectifying and stripping sections of the column.

Let us consider any one single component of the mixture. We can drop the subscripts a, b, . . . z and write for the equation of the equilibrium curve :

$$y_n = K_n x_n \qquad (1)$$

and for the operating line :

$$y_n = p x_{n+1} - a \qquad (2)$$

where p is the slope of the operating line in the section of the column under consideration, and $- a$ is the intercept of the operating line with the $x = 0$ axis.

Using equations (1) and (2), one can show that the composition on the nth plate is given by :

$$x_n = \frac{K_{n-1} K_{n-2} \ldots K_1 K_0}{p^n} x_0 + \frac{a}{p} \left(1 + \frac{K_{n-1}}{p} + \frac{K_{n-1} K_{n-2}}{p^2} + \ldots \frac{K_{n-1} K_{n-2} \ldots K_2 K_1}{p^{n-1}} \right) \qquad (3)$$

Equation (3) is basically the same as the one derived by EDMISTER [1]. Implicit in it is the usual assumption of constant molal overflow since p has been considered as a constant in the section under consideration. The equilibrium ratios K_i as shown in equation (3) are functions of temperature (at a given pressure) and of the composition. In order to obtain a convenient analytical solution, it is necessary to assume ideality of the liquid phase. This assumption makes the equilibrium ratios K_i independent of composition.

In order to evaluate analytically the products of equilibrium ratios of the type $\overset{n-1}{\underset{q}{\pi}} K_i$ entering into (3), it is necesssary to etablish some sort of relationship among the various K's. Before trying to determine the simplest suitable form of this relationship it should be noted that what determines the composition of the vapour in equilibrium with the liquid phase on an ideal plate are not the absolute values of the K's of the various components, but rather their ratios to the K of one component selected at random. These ratios, known as relative volatilities, α, are the sole factors in determining the composition of the vapour. Thus, one can write all the pertinent rectification equations in terms of α alone without the K values entering into the picture. In accordance with the practice accepted by recent contributors in the field, the relative volatilities, α, will be assumed constant in the section of the column under consideration.

From the above it becomes clear that the relationship connecting the K's of the same component on successive plates must meet only the following three requirements :

(a) It must give on every plate such values of K_i that the ratios of the K's for the various components are the correct ones.

(b) In view of the assumption of constant relative volatility the ratios of the K's must remain constant on successive plates for any given pair of components.

(c) It must contain an adjustable parameter which will make it possible to satisfy the criterion

$$\sum_a^z x_j = 1{\cdot}000.$$

A relationship which meets the above requirements is :

$$K_i = K_0\, b^{-i} \quad (i = 1, 2, 3, \ldots n - 1) \quad (4)$$

provided b is the same for all components because:

$$\frac{K_{ai}}{K_{bi}} = \frac{K_{a0}\, b_a^{-i}}{K_{b0}\, b_b^{-i}} = \frac{K_{a0}}{K_{b0}} = \alpha_{ab} = \text{constant} \quad (5)$$

or :

$$\frac{b_a^{-i}}{b_b^{-i}} = 1$$

which means that $b_a = b_b = b$ for all $i \neq 0$.

Equation (4) should therefore be looked upon only as a convenient mathematical device for meeting the requirement of correct constant value of α on every plate. How closely this equation approximates the true curve of K vs. i in the column is immaterial, and the values of K_i given by it are not and do not have to be the true ones on the successive plates. The proposed method, therefore, contains no other assumption than that of constant molal overflow and constant relative volatility and gives exact results whenever the molal overflow and the relative volatilities are constant.

With the relationship expressed in (4) the value of the products $\overset{n-1}{\underset{q}{\pi}} K_i$ is equal to :

$$\overset{n-1}{\underset{q}{\pi}} K_i = K_0^{\,n-q}\, b^{-\sum_q^{n-1} i} \quad (6)$$

$$(i = q, q + 1, q + 2 \ldots n - 2, n - 1)$$

and equation (3) may be rewritten as :

$$x_n = \frac{K_0^{\,n}\, b^{-\frac{n(n-1)}{2}}}{p^n} x_0 + \frac{a}{p}\left\{ 1 + \frac{K_0}{p} b^{-n+1} + \right.$$
$$+ \left(\frac{K_0}{p}\right)^2 b^{-2n+3} + \left(\frac{K_0}{p}\right)^3 b^{-3n+6} + \ldots +$$
$$+ \left(\frac{K_0}{p}\right)^{n-2} b^{-n(n-2) + \frac{(n-2)(n-1)}{2}} +$$
$$\left. + \left(\frac{K_0}{p}\right)^{n-1} b^{-n(n-1) + \frac{n(n-1)}{2}} \right\} \quad (7)$$

Referring all relative volatilities to component a, we have :

$$K_a = K_a ; \quad K_b = K_a\, \alpha_{ba} ;$$
$$K_c = K_a\, \alpha_{ca} ; \ldots K_z = K_a\, \alpha_{za} ;$$

and (6) when written for component z becomes :

$$\overset{i=n-1}{\underset{i=q}{\pi}} K_{zi} = (\alpha_{za}\, K_{a0})^{n-q}\, b^{-\sum_q^{n-1} i} \quad (8)$$

One can now obtain the final form of equation (7) which is :

$$x_n = Q^n\, b^{-\frac{n(n-1)}{2}} x_0 + \frac{a}{p}\left\{ 1 + Q\, b^{-n+1} + \right.$$
$$+ Q^2\, b^{-2n+3} + Q^3\, b^{-3n+6} + Q^4\, b^{-4n+10} +$$
$$+ \ldots + Q^{n-2}\, b^{-n(n-2) + \frac{(n-1)(n-2)}{2}} +$$
$$\left. + Q^{n-1}\, b^{-n(n-1) + \frac{n(n-1)}{2}} \right\} \quad (9)$$

where :

$$Q = \frac{K_{a0}\, \alpha}{p}$$

If one denotes by E_1 the expression $Q^n\, b^{-\frac{n(n-1)}{2}}$ and by E_2 the expression in the large brackets, one can rewrite (9) as follows :

$$x_n = x_0\, E_1 + \frac{a}{p} E_2 \quad (10)$$

The values of a and p are :

in stripping section: $\quad a_s = x_w\, (p_s - 1)$

$$p_s = \frac{L}{L - W}$$
(slope of operating line in stripping section)

in rectifying section: $a_r = x_d (p_r - 1)$

$$p_r = \frac{L}{L + D} = \frac{L}{V}$$

(slope of operating line in rectifying section)

Thus, if one denotes by m the number of plates in the stripping section (counted from the reboiler) and by n the number of plates in the rectifying section (counted from the feed plate,) the following equations apply :

$$x_m = x_w E_1 + \frac{x_w (p_s - 1)}{p_s} E_2 \qquad (11)$$

$$x_n = x_f E_1 + \frac{x_d (p_r - 1)}{p_r} E_2 \qquad (12)$$

If equations (11) and (12) are applied to a subsection not starting at the bottom of the stripping or rectifying sections, their form becomes :

$$x_m = x_0 E_1 + \frac{x_w (p_s - 1)}{p_s} E_2 \qquad (13)$$

$$x_n = x_0 E_1 + \frac{x_d (p_r - 1)}{p_r} E_2 \qquad (14)$$

where x_0 denotes the first plate of the subsection and m and n give the number of plates in the subsection, i.e. above x_0.

One should consider now in greater detail the functions E_1 and E_2. Both of these functions depend on Q, b, and n (or m). Table 1 gives the forms of E_1 and E_2 for m (or n) from 1 to 10. Both E_1 and E_2 can be calculated and plotted

as functions of Q with b as a parameter. Such a plot for $n = 5$ is shown in Fig. 1 on a greatly reduced scale.
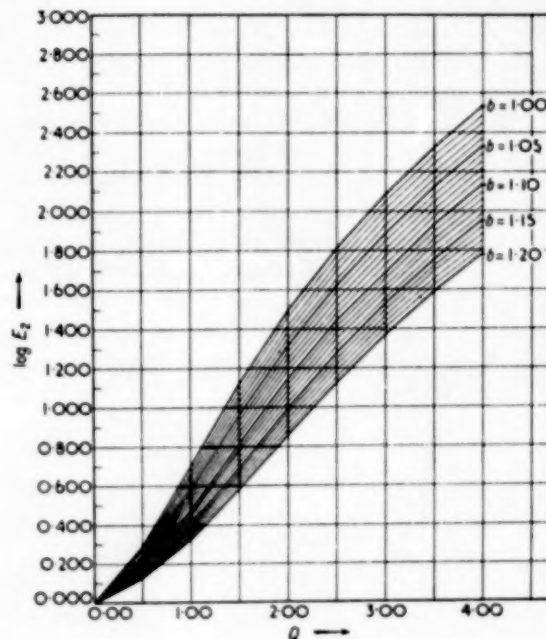
FIG. 1.

Tabulated values of E_2 for $Q = 0.5$, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0; $b = 1.0$, 1.01, 1.02, 1.03, 1.04, 1.05, 1.06, 1.07, 1.08, 1.09, 1.10, 1.15 and 1.20; $n = 2, 3, \ldots 10$ are given in Appendix I.

The method of determining the composition on plate m (or n) is relatively simple. Noting that K_{a0} is the equilibrium ratio of the component to which all the relative volatilities are referred and

Table 1. E_1 and E_2 for n or m equal to 1, 2, ... 10.

n or m	E_1	E_2
1	Q	1
2	$Q^2 b^{-1}$	$1 + Qb^{-1}$
3	$Q^3 b^{-3}$	$1 + Qb^{-2} + Q^2 b^{-3}$
4	$Q^4 b^{-6}$	$1 + Qb^{-3} + Q^2 b^{-5} + Q^3 b^{-6}$
5	$Q^5 b^{-10}$	$1 + Qb^{-4} + Q^2 b^{-7} + Q^3 b^{-9} + Q^4 b^{-10}$
6	$Q^6 b^{-15}$	$1 + Qb^{-5} + Q^2 b^{-9} + Q^3 b^{-12} + Q^4 b^{-14} + Q^5 b^{-15}$
7	$Q^7 b^{-21}$	$1 + Qb^{-6} + Q^2 b^{-11} + Q^3 b^{-15} + Q^4 b^{-18} + Q^5 b^{-20} + Q^6 b^{-21}$
8	$Q^8 b^{-28}$	$1 + Qb^{-7} + Q^2 b^{-13} + Q^3 b^{-18} + Q^4 b^{-22} + Q^5 b^{-25} + Q^6 b^{-27} + Q^7 b^{-28}$
9	$Q^9 b^{-36}$	$1 + Qb^{-8} + Q^2 b^{-15} + Q^3 b^{-21} + Q^4 b^{-26} + Q^5 b^{-30} + Q^6 b^{-33} + Q^7 b^{-35} + Q^8 b^{-36}$
10	$Q^{10} b^{-45}$	$1 + Qb^{-9} + Q^2 b^{-17} + Q^3 b^{-24} + Q^4 b^{-30} + Q^5 b^{-35} + Q^6 b^{-39} + Q^7 b^{-42} + Q^8 b^{-44} + Q^9 b^{-45}$

at the temperature of the bottom plate of the section or sub-section considered, all the Q's for the various components are computed. Thus, if a is the component to which all the relative volatilities are referred, one has :

$$Q_a = \frac{K_{a0}}{p}; \quad Q_b = \frac{K_{a0}}{p} \alpha_{ba}; \quad \ldots \quad Q_z = \frac{K_{a0}}{p} \alpha_{za}.$$

Depending on whether the stripping or rectifying section or a subsection in either is being considered one of equations (11) to (14) inclusive is written for every component. Thus if the stripping section is being considered the equations written are :

$$x_{am} = x_{aw} E_1 (Q_a, b, m) + \frac{x_{aw}(p_s-1)}{p_s} E_2 (Q_a, b, m)$$

$$----------------- (15)$$

$$x_{zm} = x_{zw} E_1 (Q_z, b, m) + \frac{x_{zw}(p_s-1)}{p_s} E_2 (Q_z, b, m)$$

The values of p and b are the same for all components.

Once equations (14) are written, one selects a value of b at random and determines from the plots of E_1 and E_2 the values of these two functions for each component and for the particular value of m (or n). These values of E_1 and E_2 are used in equations (15) and x_{am}, x_{bm}, $\ldots x_{zm}$ calculated. If these satisfy the condition

$$\sum_a^z x_j = 1 \cdot 000 \tag{16}$$

then the value of b used was the right one and the concentrations x_{am}, x_{bm}, etc., are the correct ones. If (16) is not satisfied, a new value of b is selected and E_1 and E_2 corresponding to this new value are read off the charts. The calculation may thus have to be repeated several times before the value of b which satisfies (16) is obtained. The process is a very rapid one, however, since on every trial the only variable terms are E_1 and E_2 while the coefficients in front of them remain the same.

The present paper gives values of E_2 for n from 1 to 10. This limits at present the number of plates which can be considered at a time to 10. It is possible, however, to extend in the future the range of known values of E_2 and thus make possible the calculation of 20, 30 or more plates in a single step. In general the values of p and α cannot be considered constant in sections containing more than ten plates except, perhaps, in some very difficult separations. It is advisable, therefore, for greater accuracy to calculate the column in subsections of ten plates, check the temperature and reflux conditions prevailing on that plate and use the new values of p and α thus determined in the calculation of the next subsection. It should be noted that in order to calculate K_{a0} at the plate on the bottom of the following subsection (equal to K_{am} at the top plate of the preceding subsection) one should not use the formula given in (4), but rather calculate the temperature on the plate and use K_{am} corresponding to this temperature. The reason for this is that, as previously explained, equation (4) does not necessarily give the correct values of the K_i's but only the correct values of α.

The value of b is not necessarily the same for two consecutive subsections. The component to which all relative volatilities are referred should be one of intermediate volatility so that it is present in significant amounts in both ends of the section (or subsection considered).

One of the basic difficulties in multicomponent rectification calculations is the impossibility to fix all terminal composition once the feed composition and the reflux ratio have been fixed. (For detailed discussion of this aspect of multicomponent rectification see ref. 7). This difficulty of uncertain terminal composition arises from phase rule considerations and no method can ever hope to overcome them. All present methods handle them by making reasonable assumptions as to the concentrations in the terminal streams, and checking these assumptions against the results obtained. The method proposed in this paper should be used in the same manner.

Minimum number of plates

For this special case $p = 1$ and equations (11) and (12) become :

$$x_m = x_w E_1 = x_w Q^m b^{-\frac{m(m-1)}{2}} \tag{17}$$

$$x_n = x_f E_1 = x_w Q^n b^{-\frac{n(n-1)}{2}}$$

In determining the minimum number of plates required in order to reach a certain composition both x_m and x_w (or x_n or x_f) are given, and (17) may be rewritten as :

$$b = \left[\frac{x_w}{x_m} Q^m\right] - \frac{2}{m(m-1)} \quad \text{in stripping section}$$

$$b = \left[\frac{x_f}{x_n} Q^n\right] - \frac{2}{n(n-1)} \quad \text{in rectifying section} \qquad (18)$$

Equations of the type of (18) may be written for every component and since b is the same for all components, one obtains :

$$\overset{\text{I}}{\left(\frac{x_{af}}{x_{an}}\right)} = \overset{\text{II}}{\left(\frac{x_{bf}}{x_{bn}} \alpha_{ba}^{\cdot n}\right)} = \ldots = \left(\frac{x_{zf}}{x_{zn}} \alpha_{za}^{n}\right) \qquad (19)$$

It can be shown that in the case of only two components equation (19) is identical to the Fenske equation.

One can take I and II and solve directly and easily for the unknown n. Then in a similar way take II and III, III and IV, etc. If the values of n thus obtained differ considerably, it shows that it is impossible to obtain at total reflux the concentrations x_{an}, x_{bn}, ... x_{zn} starting with the concentrations x_{af}, x_{bf} . . . . . x_{zf}. A readjustment of one of the terminal streams is then made and the calculation repeated at least until n for the important pairs of components is the same. Since the number of plates at minimum reflux is directly determinable from the desired separation of the keys, the important pairs of components are clearly the key components. The illustrative example shows the manner in which the minimum number of plates is obtained, or conversely the manner in which the composition on the nth plate at total reflux is determined.

Minimum reflux ratio

Determination of the minimum reflux ratio in multi-component rectification is one of the most difficult aspects of the general problem. Equations (11) and (12) can presumably be used with successively decreasing values of p_r or increasing values of p_s until a value of p_r (or p_s) is reached which satisfies the criterion for minimum reflux. Since p, however, enters in both E_1 and E_2 as well as in the coefficient in front of E_2 (Eq. 11)

and 12), the procedure is slow, and the present method is not recommended specially in the presence of other excellent methods for obtaining the minimum reflux ratio [4, 5].

Example No. 1

As a first example we shall consider the tar acid fractionation problem solved by plate-to-plate calculations by ROBINSON and GILLILAND [7], p. 236.

The composition of the waste, feed, and distillate streams are as follows :

	Waste	Feed	Distillate
x_a	0·0524	0·350	0·9530
x_b	0·2020	0·150	0·0455
x_0	0·4470	0·300	0·0015
x_d	0·2240	0·150	
x_e	0·0750	0·050	

The slope of the operating line in the stripping section is 1·184 and in the rectifying section 0·9091. The temperature in the reboiler is 160°C and at this temperature, the relative volatilities are :

$\alpha_{ab} = 1·25$; $\alpha_{bb} = 1·00$; $\alpha_{cb} = 0·70$; $\alpha_{db} = 0·44$; $\alpha_{eb} = 0·087$. K_b at 160°C is 1·46.

Since the purpose of this example is to compare the results of the present method with the rigorous stepwise method, the procedure used by ROBINSON and GILLILAND will be followed closely. Thus, since these two authors change the values of α on the 8th plate above the reboiler, a subsection starting with the still pot and including the 8th plate above it will be calculated first.

$$Q_a = \frac{K_b x_{ab}}{p} = \frac{1·46}{1·184} \times 1·25 \quad = 1·231 \times 1·25 \quad = 1·54$$
$$Q_b \qquad\qquad\qquad\qquad = 1·231 \times 1·00 \quad = 1·231$$
$$Q_c \qquad\qquad\qquad\qquad = 1·231 \times 0·70 \quad = 0·862$$
$$Q_d \qquad\qquad\qquad\qquad = 1·231 \times 0·44 \quad = 0·542$$
$$Q_e \qquad\qquad\qquad\qquad = 1·231 \times 0·087 = 0·107$$

Equations (11) for all component on the 8th plate becomes :

$x_{a8} = 0·0524 \, E_1 (1·54, \ b, 8) + 0·008153 \, E_2 (1·54, \ b, 8)$
$x_{b8} = 0·202 \, E_1 (1·231, b, 8) + 0·03143 \, E_2 (1·231, b, 8)$
$x_{c8} = 0·447 \, E_1 (0·862, b, 8) + 0·06947 \, E_2 (0·862, b, 8)$
$x_{d8} = 0·224 \, E_1 (0·542, b, 8) + 0·03485 \, E_2 (0·542, b, 8)$
$x_{e8} = 0·075 \, E_1 (0·107, b, 8) + 0·01167 \, E_2 (0·107, b, 8)$

By trial and error it is found that $\overset{e}{\underset{a}{\sum}} x_J = 1\cdot00$ when $b = 1\cdot066$. Substituting the values of E_1 and E_2 at $b = 1\cdot066$ in the above equations, one obtains the composition in the 8th plate :

$$x_{a8} = 0\cdot0524 \times 5\cdot250 + 0\cdot008153 \qquad\qquad \text{R. and G.}$$
$$\qquad \times 13\cdot32 = 0\cdot2751 + 0\cdot1084 = 0\cdot3835 \qquad 0\cdot375$$
$$x_{b8} = 0\cdot202 \times 0\cdot8806 + 0\cdot03143$$
$$\qquad \times 5\cdot59 = 0\cdot1779 + 0\cdot1757 = 0\cdot3536 \qquad 0\cdot355$$
$$x_{c8} = 0\cdot447 \times 0\cdot0508 + 0\cdot06947$$
$$\qquad \times 2\cdot46 = 0\cdot0227 + 0\cdot1711 = 0\cdot1938 \qquad 0\cdot204$$
$$x_{d8} = 0\cdot224 \times 0 + 0\cdot03485 \times 1\cdot59 \quad = 0\cdot0552 \qquad 0\cdot056$$
$$x_{e8} = 0\cdot075 \times 0 + 0\cdot01167 \times 1\cdot16 \quad = 0\cdot0135 \qquad 0\cdot013$$

$$x = 0\cdot9996 \qquad x = 1\cdot003$$

The temperature on the 8th plate may be found to be 120°C and ROBINSON and GILLILAND use the following values of the relative volatilities for the next subsection :

$$\alpha_{ab} = 1\cdot26; \ \alpha_{bb} = 1\cdot00; \ \alpha_{cb} = 0\cdot675; \ \alpha_{db} = 0\cdot392;$$
$$\alpha_{eb} = 0\cdot087. \ K_{b8} \ (\text{at } 120°\text{C}) = 1\cdot013.$$

With these values of α and K_{b8} the Q's for each component are calculated and one can write for the composition of the 5th plate of the subsection which starts at the 8th plate above the reboiler (i.e. the 13th plate counting from the reboiler) the following set of equations :

$$x_{a5} = 0\cdot3835 \ E_1 \ (1\cdot078, \ b, 5) + 0\cdot008153 \ E_2 \ (1\cdot078, \ b, 5)$$
$$x_{b5} = 0\cdot3536 \ E_1 \ (0\cdot8553, b, 5) + 0\cdot03143 \quad E_2 \ (0\cdot8553, b, 5)$$
$$x_{c5} = 0\cdot1938 \ E_1 \ (0\cdot5773, b, 5) + 0\cdot06947 \quad E_2 \ (0\cdot5773, b, 5)$$
$$x_{d5} = 0\cdot0552 \ E_1 \ (0\cdot3353, b, 5) + 0\cdot03485 \quad E_2 \ (0\cdot3353, b, 5)$$
$$x_{e5} = 0\cdot0135 \ E_1 \ (0\cdot0744, b, 5) + 0\cdot01167 \quad E_2 \ (0\cdot0744, b, 5)$$

After several trials it is found that the value of b which satisfies $\overset{e}{\underset{a}{\sum}} x_J = 1\cdot0$ is $b = 1\cdot015$. With this value of b, the functions E_1 and E_2 are read off the charts, substituted in the above equations and the composition on the 5th plate of the subsection obtained :

	Robinson and Gilliland
$x_{a13} = 0\cdot5242$	$0\cdot525$
$x_{b13} = 0\cdot2527$	$0\cdot252$
$x_{c13} = 0\cdot1601$	$0\cdot160$
$x_{d13} = 0\cdot0528$	$0\cdot0514$
$x_{e13} = 0\cdot0126$	$0\cdot0126$
$\sum x = 1\cdot0024$	$\sum x = 1\cdot0010$

Because of the fact that the ratio of the concentrations of componnet a to component b in the liquid on the 13th plate is essentially that of the feed, ROBINSON and GILLILAND consider the 13th plate as the feed plate. The same will be done in the present example. In the rectifying section $p_r = 0\cdot9091$ and $K_{b,13} = 0\cdot9605$.

$$Q_a = \frac{K_b x_{ba}}{p} = \frac{0\cdot9605}{0\cdot9091} x_{ab} = 1\cdot0565 x_{ab} = 1\cdot0565 \times 1\cdot26 = 1\cdot3312$$
$$Q_b = \qquad\qquad\qquad\qquad\qquad 1\cdot0565 = 1\cdot00 = 1\cdot0565$$
$$Q_c = \qquad\qquad\qquad\qquad\qquad 1\cdot0565 \times 0\cdot675 = 0\cdot7131$$
$$Q_d = \qquad\qquad\qquad\qquad\qquad 1\cdot0565 \times 0\cdot392 = 0\cdot4141$$
$$Q_e = \qquad\qquad\qquad\qquad\qquad 1\cdot0565 \times 0\cdot087 = 0\cdot0919$$

$$x_{an} = 0\cdot5242 \ E_1 \ (1\cdot3312, b, n) - 0\cdot0953 \quad E_2 \ (1\cdot3312, b, n)$$
$$x_{bn} = 0\cdot2527 \ E_1 \ (1\cdot0565, b, n) - 0\cdot00455 \ E_2 \ (1\cdot0565, b, n)$$
$$x_{cn} = 0\cdot1601 \ E_1 \ (0\cdot7131, b, n) - 0\cdot00015 \ E_2 \ (0\cdot7131, b, n)$$
$$x_{dn} = 0\cdot0528 \ E_1 \ (0\cdot4141, b, n) - 0 \quad \times \quad E_2 \ (0\cdot4141, b, n)$$
$$x_{en} = 0\cdot0126 \ E_1 \ (0\cdot0919, b, n) - 0 \quad \times \quad E_2 \ (0\cdot0919, b, n)$$

To calculate the composition on the 10th plate above the feed plate (23rd above the reboiler) one uses the values of the functions E_1 and E_2 at $n = 10$. The value of b which satisfies $\overset{e}{\underset{a}{\sum}} x_J = 1\cdot000$ is $b = 1\cdot0257$. The equations for this plate then become :

$$x_{a,10} = 0\cdot5242 \times 5\cdot578 \qquad\qquad\qquad \text{R. and G.}$$
$$\qquad\qquad - 0\cdot0953 \times 21\cdot38 = 0\cdot8865 \qquad 0\cdot896$$
$$x_{b,10} = 0\cdot2527 \times 0\cdot5532$$
$$\qquad\qquad - 0\cdot00455 \times 6\cdot871 = 0\cdot1084 \qquad 0\cdot102$$
$$x_{c,10} = 0\cdot1601 \times 0\cdot01085$$
$$\qquad\qquad - 0\cdot00015 \times 2\cdot483 = 0\cdot0013 \qquad 0\cdot0007$$
$$x_{d,10} = 0\cdot0528 \times 0\cdot00004 \qquad = 0\cdot0000 \qquad 0\cdot000$$
$$x_{e,10} = 0\cdot0126 \times 0 \qquad\qquad = 0\cdot0000 \qquad 0\cdot0000$$

$$\sum x = 0\cdot9962 \qquad \sum x = 0\cdot9987$$

Next one can calculate the subsection included between the 10th and 13th plate above the feed (23rd to 26th plate above the reboiler.) The new values of Q are :

$$Q_a = \frac{K_{b23} x_{ab}}{p_r} = \frac{0\cdot8111}{0\cdot9091} x_{ab} = 0\cdot8922 x_{ab} = 0\cdot8922 \times 1\cdot26 = 1\cdot1242$$
$$Q_b = \qquad\qquad\qquad\qquad\qquad\qquad = 0\cdot8922 \times 1\cdot00 = 0\cdot8922$$
$$Q_c = \qquad\qquad\qquad\qquad\qquad\qquad = 0\cdot8922 \times 0\cdot675 = 0\cdot6022$$

The composition on the 13th plate above the feed is given by .

$$x_a = 0\cdot8865 \ E_1 \ (1\cdot1242, b, 3) - 0\cdot0953 \quad E_2 \ (1\cdot1242, b, 3)$$
$$x_b = 0\cdot1084 \ E_1 \ (0\cdot8922, b, 3) - 0\cdot00455 \ E_2 \ (0\cdot8922, b, 3)$$
$$x_c = 0\cdot0013 \ E_1 \ (0\cdot6022, b, 3) - 0\cdot00015 \ E_2 \ (0\cdot6022, b, 3)$$

The value of b which gives $\overset{e}{\underset{a}{\sum}} x_J = 1\cdot000$ is $b = 1\cdot00$ and with this value one obtains :

$x_a = 0\cdot8865 \times 1\cdot4208 - 0\cdot0953$ R. and G.
$\times 3\cdot8880 = 1\cdot2595 - 0\cdot3229 = 0\cdot9366$ 0·942
$x_b = 0\cdot1084 \times 0\cdot7102 - 0\cdot00455$
$\times 2\cdot6882 = 0\cdot0770 - 0\cdot0122 = 0\cdot0648$ 0·058
$x_c = 0\cdot0013 \times 0\cdot2184 - 0\cdot00015$
$\times 1\cdot9648 = 0\cdot00029 - 0\cdot00029 = 0\cdot0000$ 0·000

$\Sigma x = 1\cdot0014$ $\Sigma x = 1\cdot000$

The vapour rising from the 26th plate upon condensation gives the desired distillate composition, and the column therefore has 25 plates, 13 in each rectifying and stripping section. The answer in the above example was obtained in four trial-and-error steps instead of the 26 such steps of the rigorous step-wise calculation. The considerable saving in time is thus obvious. The relationship between the actual values of the

FIG. 2.

volatility ratio and those given by $K_i = K_0 \times 1\cdot066^{-i}$ is shown on Fig. 2.

Example No. 2.   Minimum number of Plates

Consider the following five components under total reflux :

Component	x_w	α	x_n (assumed)
a	0·0524	1·25	0·585
b	0·202	1·00	0·376
c	0·447	0·70	0·021
d	0·224	0·44	0·018
e	0·075	0·087	0·000

What is the minimum number of plates required to obtain the composition x_n (assumed) ?

From equation (19) we have :

$$\underset{\text{I}}{\left(\frac{0\cdot0524}{0\cdot585} \times 1\cdot25^n\right)} \overset{?}{=} \underset{\text{II}}{\left(\frac{0\cdot202}{3\cdot376} \times 1\cdot00^n\right)} \overset{?}{=}$$

$$\overset{?}{=} \underset{\text{III}}{\left(\frac{0\cdot447}{0\cdot021} \times 0\cdot70^n\right)} \overset{?}{=} \underset{\text{IV}}{\left(\frac{0\cdot224}{0\cdot018} \times 0\cdot44^n\right)}$$

From I and II : $n = 8$
From II and III : $n = 10\cdot4$
From III and IV : $n < 0$

Clearly the assumed concentrations cannot be obtained under conditions of total reflux and the composition on the nth plate should be readjusted.

If we consider components a and b as the important ones and do not wish to change x_{an} and x_{bn}, we can calculate readily the change necessary in the assumed values of x_c and x_d in order to obtain a composition compatible with the starting composition under total reflux. Thus solving II and III together with $n = 8$ we obtain :

$$\underset{\text{II}}{\left(\frac{0\cdot202}{0\cdot376} \times 1\cdot00^8\right)} = \underset{\text{III}}{\left(\frac{0\cdot447}{x_{cn}} \times 0\cdot70^8\right)}$$

$$\therefore x_{cn} = 0\cdot048$$

From II and IV :

$$\left(\frac{0\cdot202}{0\cdot376} \times 1\cdot00^8\right) = \left(\frac{0\cdot224}{x_{dn}} \times 0\cdot44^8\right)$$

$$\therefore x_{dn} = 0\cdot0006$$

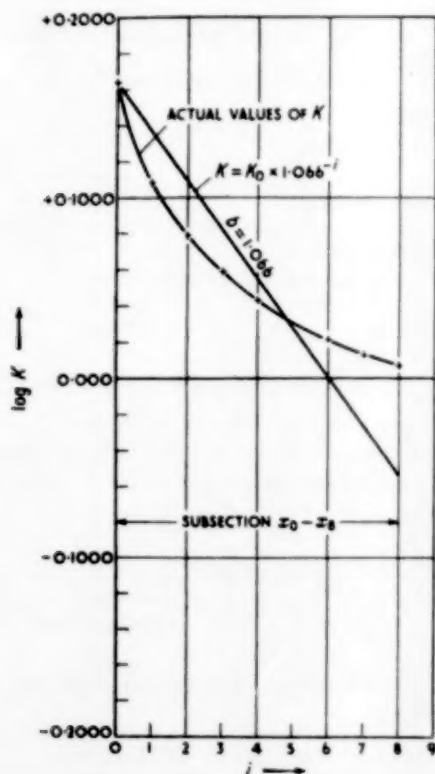The results are summarized and compared with these obtained by stepwise calculations follows :

n = 2

b	Q = 0·50	Q = 1·00	Q = 1·50	Q = 2·00	Q = 2·50	Q = 3·00	Q = 3·50	Q = 4·00
1·00	1·500	2·000	2·500	3·000	3·500	4·000	4·500	5·000
1·01	1·495	1·990	2·485	2·980	3·475	3·970	4·465	4·960
1·02	1·490	1·980	2·471	2·961	3·451	3·941	4·431	4·922
1·03	1·485	1·971	2·456	2·942	3·427	3·913	4·398	4·884
1·04	1·481	1·962	2·442	2·923	3·404	3·885	4·366	4·846
1·05	1·476	1·952	2·429	2·905	3·381	3·857	4·333	4·810
1·06	1·472	1·943	2·415	2·887	3·358	3·830	4·302	4·774
1·07	1·467	1·935	2·402	2·869	3·336	3·804	4·271	4·738
1·08	1·463	1·926	2·388	2·852	3·315	3·778	4·241	4·704
1·09	1·459	1·917	2·376	2·835	3·294	3·752	4·211	4·670
1·10	1·455	1·908	2·364	2·818	3·273	3·727	4·182	4·636
1·15	1·435	1·870	2·307	2·739	3·174	3·609	4·044	4·478
1·20	1·417	1·833	2·250	2·667	3·083	3·500	3·917	4·333

n = 3

b	Q = 0·50	Q = 1·00	Q = 1·50	Q = 2·00	Q = 2·50	Q = 3·00	Q = 3·50	Q = 4·00
1·00	1·750	3·000	4·750	7·000	9·750	13·00	16·75	21·00
1·01	1·733	2·951	4·654	6·843	9·517	12·68	16·32	20·45
1·02	1·716	2·904	4·562	6·692	9·292	12·36	15·91	19·92
1·03	1·700	2·858	4·473	6·546	9·076	12·06	15·50	19·41
1·04	1·684	2·814	4·387	6·405	8·878	11·77	15·13	18·92
1·05	1·669	2·771	4·304	6·269	8·666	11·50	14·76	18·45
1·06	1·655	2·730	4·224	6·138	8·472	11·23	14·40	17·99
1·07	1·641	2·690	4·147	6·012	8·286	10·97	14·06	17·55
1·08	1·627	2·651	4·072	5·890	8·105	10·72	13·72	17·13
1·09	1·614	2·614	4·000	5·772	7·930	10·47	13·40	16·72
1·10	1·601	2·578	3·930	5·658	7·762	10·24	13·10	16·32
1·15	1·542	2·414	3·614	5·142	7·000	9·186	11·70	14·54
1·20	1·492	2·273	3·344	4·704	6·353	8·292	10·52	13·04

n = 4

b	Q = 0·50	Q = 1·00	Q = 1·50	Q = 2·00	Q = 2·50	Q = 3·00	Q = 3·50	Q = 4·00
1·00	1·875	4·000	8·125	15·00	25·37	40·00	59·63	85·00
1·01	1·841	3·864	7·776	14·28	24·09	37·91	56·45	80·40
1·02	1·809	3·736	7·448	13·61	22·89	35·95	53·47	76·09
1·03	1·778	3·615	7·140	12·98	21·76	34·12	50·68	72·06
1·04	1·749	3·501	6·851	12·39	20·71	32·40	48·07	68·29
1·05	1·721	3·394	6·577	11·83	19·71	30·79	45·62	64·75
1·06	1·695	3·292	6·320	11·31	18·78	29·28	43·32	61·43
1·07	1·670	3·196	6·078	10·82	17·91	27·86	41·17	58·32
1·08	1·646	3·105	5·849	10·35	17·08	26·52	39·14	55·40
1·09	1·623	3·018	5·633	9·914	16·30	25·26	37·23	52·64
1·10	1·601	2·937	5·429	9·503	15·58	24·08	36·57	50·07
1·15	1·507	2·587	4·564	7·763	12·50	19·12	27·93	39·25
1·20	1·432	2·316	3·903	6·444	10·19	15·40	22·31	31·18

n = 5

b	Q = 0·50	Q = 1·00	Q = 1·50	Q = 2·00	Q = 2·50	Q = 3·00	Q = 3·50	Q = 4·00
1·00	1·937	5·000	13·19	31·00	64·43	121·0	209·8	341·0
1·01	1·885	4·713	12·21	28·45	58·88	110·3	190·9	310·0
1·02	1·835	4·432	11·32	26·15	53·87	102·0	173·8	282·2
1·03	1·790	4·212	10·52	24·06	49·33	93·75	158·6	257·1
1·04	1·747	3·993	9·783	22·18	45·25	86·28	144·8	234·5
1·05	1·708	3·792	9·116	20·47	41·55	76·99	132·4	214·1
1·06	1·671	3·607	8·508	18·91	38·19	73·28	121·1	195·8
1·07	1·637	3·438	7·955	17·50	35·16	67·64	110·9	179·0
1·08	1·605	3·282	7·449	16·22	32·39	62·49	101·7	163·9
1·09	1·575	3·138	6·985	15·05	29·88	57·77	93·32	150·2
1·10	1·547	3·006	6·562	13·98	27·60	48·51	85·74	137·8
1·15	1·431	2·479	4·914	9·876	18·87	33·79	56·93	90·77
1·20	1·345	2·117	3·823	7·215	13·28	23·27	38·66	61·14

n = 6

b	Q = 0·50	Q = 1·00	Q = 1·50	Q = 2·00	Q = 2·50	Q = 3·00	Q = 3·50	Q = 4·00
1·00	1·969	6·000	20·78	63·00	162·1	364·0	734·9	1,365
1·01	1·897	5·485	18·42	55·14	141·1	315·8	636·6	1,181
1·02	1·831	5·032	16·38	48·37	123·0	274·5	552·2	1,023
1·03	1·772	4·633	14·60	42·52	107·4	238·9	479·8	888·0
1·04	1·718	4·282	13·06	37·46	92·99	208·4	417·6	772·0
1·05	1·669	3·970	11·71	33·07	82·38	182·0	363·9	671·9
1·06	1·624	3·695	9·536	29·26	72·34	159·2	317·6	585·7
1·07	1·584	3·452	9·509	25·96	63·67	139·5	277·7	511·5
1·08	1·547	3·234	8·605	23·08	56·12	122·5	243·4	447·2
1·09	1·512	3·040	7·810	20·56	49·55	107·6	213·2	391·4
1·10	1·480	2·867	7·113	18·36	43·85	94·79	187·3	342·2
1·15	1·356	2·232	4·665	10·77	23·46	51·40	99·99	181·5
1·20	1·270	1·851	3·305	6·800	14·35	29·06	55·37	99·30

n = 7

b	Q = 0·50	Q = 1·00	Q = 1·50	Q = 2·00	Q = 2·50	Q = 3·00	Q = 3·50	Q = 4·00
1·00	1·984	7·000	32·17	127·0	406·2	1,093	2,573	5,461
1·01	1·893	6·167	27·04	104·9	333·2	893·6	2,100	4,451
1·02	1·813	5·468	22·82	86·90	274·0	732·2	1,717	3,636
1·03	1·742	4·880	19·35	72·30	225·8	601·3	1,407	2,976
1·04	1·679	4·384	16·49	60·22	186·7	495·1	1,156	2,442
1·05	1·617	3·981	14·11	50·36	154·7	408·4	951·4	2,006
1·06	1·572	3·605	12·14	42·26	131·5	337·6	784·6	1,651
1·07	1·528	3·300	10·50	35·60	107·0	279·9	648·7	1,364
1·08	1·487	3·038	9·134	30·09	89·42	232·5	537·5	1,127
1·09	1·431	2·812	7·985	25·52	74·86	193·5	446·0	934·6
1·10	1·418	2·618	7·022	21·73	62·87	161·5	370·9	775·9
1·15	1·293	1·965	4·024	10·35	27·43	67·65	152·2	314·8
1·20	1·213	1·620	2·660	5·553	13·01	30·18	65·84	133·9

$n = 8$

b	$Q = 0.50$	$Q = 1.00$	$Q = 1.50$	$Q = 2.00$	$Q = 2.50$	$Q = 3.00$	$Q = 3.50$	$Q = 4.00$
1.00	1.992	8.000	49.261	255.00	1,016.6	3,280.0	9,006.9	21,845
1.01	1.883	6.752	38.830	196.69	778.05	2,501.5	6,856.1	16,609
1.02	1.789	5,760	30.801	152.31	597.36	1,913.3	5,233.3	12,662
1.03	1.708	4.968	24.596	118.42	460.09	1,471.6	4,005.4	9,678.7
1.04	1.638	4.332	19.794	92.520	355.74	1,129.6	3,075.9	7,422.4
1.05	1.577	3.817	16.048	72.579	275.86	871.70	2,366.7	5,705.3
1.06	1.523	3.397	13.111	57.203	214.64	674.64	1,827.6	4,396.9
1.07	1.476	3.055	10.813	45.338	167.70	523.96	1,415.2	3,399.2
1.08	1.434	2.773	8.994	36.104	131.42	407.94	1,098.4	2,633.6
1.09	1.397	2.538	7.552	28.912	103.37	318.54	854.70	2,045.4
1.10	1.369	2.344	6.421	23.329	81.726	249.84	667.76	1,594.7
1.15	1.243	1.739	3.271	8.7922	26.813	77.408	201.62	475.12
1.20	1.169	1.452	2.114	4.1015	10.083	26.286	65.373	150.59

$n = 9$

b	$Q = 0.50$	$Q = 1.00$	$Q = 1.50$	$Q = 2.00$	$Q = 2.50$	$Q = 3.00$	$Q = 3.50$	$Q = 4.00$
1.00	1.996	9.000	74.89	511.0	2,542	9,841	31,530	87,370
1.01	1.869	7.236	54.79	364.3	1,797	6,931	22,160	61,350
1.02	1.764	5.916	40.43	261.0	1,274	4,900	15,630	43,220
1.03	1.674	4.923	30.12	188.0	909.1	3,477	11,070	30,560
1.04	1.599	4.171	22.84	137.7	659.6	2,515	7,997	22,070
1.05	1.534	3.583	17.29	99.24	467.8	1,771	5,609	14,740
1.06	1.478	3.132	13.34	72.78	337.7	1,271	4,014	11,030
1.07	1.429	2.778	10.44	53.79	245.1	916.3	2,885	7,918
1.08	1.387	2.498	8.290	40.02	178.5	662.2	2,078	5,692
1.09	1.350	2.274	6.685	30.02	130.7	480.5	1,502	4,106
1.10	1.318	2.093	5.483	22.74	96.27	350.5	1,091	2,975
1.15	1.203	1.568	2.603	6.745	22.89	76.84	231.4	621.5
1.20	1.136	1.338	1.738	2.910	6.873	19.37	54.29	141.2

$n = 10$

b	$Q = 0.50$	$Q = 1.00$	$Q = 1.50$	$Q = 2.00$	$Q = 2.50$	$Q = 3.00$	$Q = 3.50$	$Q = 4.00$
1.00	1.998	10.00	113.3	1,023	6,358	29,520	110,300	349,400
1.01	1.854	7.616	76.14	667.2	4,109	19,010	70,920	224,400
1.02	1.738	5.951	51.74	437.8	2,669	12,300	45,790	144,700
1.03	1.641	4.772	35.63	289.1	1,743	7,994	29,690	93,680
1.04	1.562	3.927	24.92	192.4	1,145	5,215	19,360	60,990
1.05	1.494	3.310	17.72	129.0	754.7	3,426	12,660	39,830
1.06	1.437	2.853	12.84	87.14	500.6	2,257	8,315	26,120
1.07	1.389	2.511	9.520	59.51	334.2	1,496	5,492	17,220
1.08	1.347	2.250	7.219	41.02	224.1	994.1	3,637	11,380
1.09	1.311	2.047	5.622	28.69	151.7	666.0	2,426	7,575
1.10	1.279	1.888	4.488	20.28	103.0	446.6	1,618	5,043
1.15	1.171	1.446	2.110	4.834	17.27	66.06	231.4	708.3
1.20	1.110	1.259	1.504	2.127	4.322	12.23	37.73	110.2

Carbon tetrachloride/Acetic acid azeotrope

The effect of pressure on the composition of the azeotrope

C. O. HAUGHTON

Courtaulds Ltd , Research Laboratories, Coventry

Summary—A method is described for determining the composition of the carbon tetrachloride/ acetic acid azeotrope at pressures within the range 10-1,000 mm Hg absolute. Reduction in pressure decreases the percentage of acetic acid in the azeotrope. The composition at 760 mm absolute is found to be 1·54% acetic acid by weight which is lower than previously reported values.

Résumé—L'auteur décrit une méthode pour déterminer la composition de l'azéotrope du mélange acide acétique – tétrachlorure de carbone par une échelle des pressions de 10 à 1000 mm de mercure. L'abaissement de la pression diminue le pourcentage d'acide acétique dans l'azéotrope. La composition à 760 mm absolus est de 1,54% en poids d'acide acétique, plus basse que les valeurs précédemment indiquées.

INTRODUCTION

The existence of an azeotrope of carbon tetrachloride and acetic acid boiling at 76·5°C under 760 mm Hg absolute pressure and containing 3·0% acetic acid by weight has been reported by M. LECAT [1] and is published in the list of azeotropes complied by L. H. HORSLEY [2].

The work described in this article was carried out to determine the effect of pressure on the composition of the azeotrope over the range 10-1,000 mm Hg absolute.

EXPERIMENTAL METHOD

Six mixtures A-F were made up containing 400 g of pure carbon tetrachloride and approximately 0·5, 2, 4, 6, 8 and 10 grams respectively of glacial acetic acid (99·8% by freezing point). These mixtures were distilled in turn from a 500 ml. flask through a Dufton spiral glass fractionating column 9·0 inches high × 1·0 inches diameter, still head, and condenser, the distillates being collected in a receiver. All connections were made with ground glass joints. The receiver had a side arm connected to a source of vacuum and a mercury manometer.

Each distillation was carried out at atmospheric pressure and at three or four different reduced
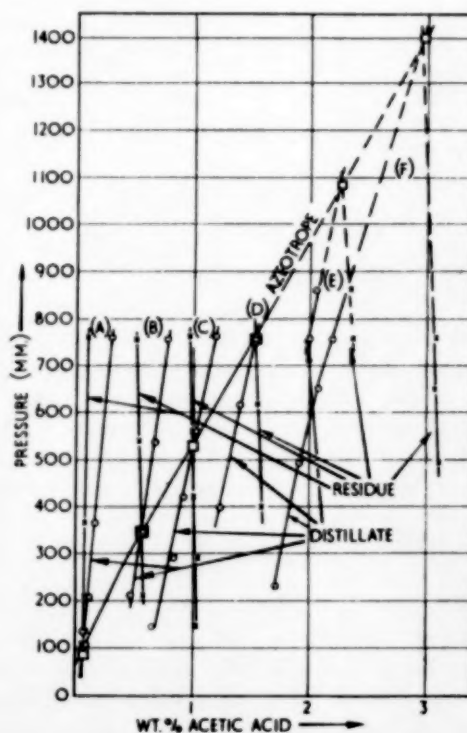

FIG. 1. Effect of pressure on the composition of carbon tetrachloride—acetic acid azeotrope.

Table I. *Acetic acid contents of distillates and residues from mixtures A-F.*

	Pressure (mm)	B.P. (°C)	Mls distilled	Weight % acetic acid in	
				distillate	residue
MIXTURE A	761	76·0	12	·310	·107
	364	53·7	19	·173	·084
	211	39·0	15	·119	·078
	137	29	22	·084	·071
	112	24	18	·079	·073
MIXTURE B	753	75·6	15	·798	·535
	538	65·0	24	·687	·550
	347	52·5	37	·565	·557
	209	38·8	29	·470	·573
MIXTURE C	764	76·0	27	1·20	0·98
	559	66·0	14	1·02	1·01
	421	57·7	16	0·93	1·02
	288	47·1	24	0·83	1·03
	144	—	12	0·65	1·02
MIXTURE D	753	75·6	17	1·54	1·54
	614	69·2	22	1·41	1·56
	397	56·4	2	1·23	1·60
MIXTURE E	753	75·8	15	2·01	2·39
	860	80·8	—	2·07	2·37
MIXTURE F	753	75·8	40	2·20	3·10
	648	—	20	2·08	3·08
	491	62·6	20	1·92	3·12
	231	41·5	30	1·71	—

pressures. About 20 ml. of distillate were collected at each pressure and the distillate and residue were both analysed by titration of 5 or 10 ml. with 0·1 N sodium hydroxide. The compositions of distillates and residues were plotted against pressure and the point where the two curves intersected was taken as the composition of the azeotrope.

Results

The results of the six series of distillations are given in Table I and the distillate and residue compositions are plotted against pressure in the figure. A curve drawn through the points where the distillate-residue compositions intersect gives the composition of the azeotrope.

Table II. *Composition and boiling point of azeotrope.*

Press (mm)	B.P. (°C)	Weight % acetic acid
1400	—	3·0
1080	90	2·30
760	76·0	1·54
530	64·6	1·00
340	51·5	0·58
90	18·7	0·72

In experiments E and F intersections of the distillate and residue composition lines lay outside the operating pressure range of the

apparatus and had therefore to be found by extrapolation, with consequent reduction in the accuracy of the results.

The boiling points of the six azeotropes thus established have been obtained from the temperature-pressure data in Table I by plotting boiling point against pressure for each of the mixtures A-F and reading from the curves the boiling point of the azeotrope at its corresponding pressure. Table 2 gives the composition and boiling point of the azeotrope thus found.

CONCLUSIONS

1. The composition of the carbon tetra-chloride-acetic acid azeotrope at atmospheric pressure is 1·54% acetic acid by weight. This disagrees with the previously reported figure of 3% by weight published by LECAT [1].

2. Reduced pressure decreases the percentage acid in the carbon tetrachloride/acetic acid. From the slope of the curve in Fig. 1 it would appear that an azeotrope is no longer formed at pressures below about 50 mm Hg absolute.

ACKNOWLEDGMENT

REFERENCES

[1]   LECAT, M.; *Ann. Soc. Sci. Bruzelles*, (1929), **49B**, (I) 109.

[2]   HORSLEY, L. H.; Azeotropic data. *Ann. Chem. Soc.* (June), 1952.

Book reviews

H. MIESSNER and U. GRIGULL (Editors) : Fortschritte der Verfahrenstechnik 1952/53. (Progress in Process Technique in 1952-53), Verlag Chemie, GMBH, Weinhem-Bergstr. 1954. 496 pages. Price DM 39.

THIS is the first volume of a proposed series, with succeeding volumes to be published by the Farbenfabriken Bayer at intervals of one to two years, in which an attempt will be made to review and summarize the literature concerned with unit operations and process techniques. In general each volume will be limited to the literature which has appeared since publication of the preceding volume, although in the first volume references are made to works published before the period of 1952-53. The book is divided into sections covering the usual unit operations, such as fluid flow, heat transfer, gas absorption, and distillation ; the techniques involved in the use of high temperatures, low temperatures, high pressures, and vacua ; and reactors, materials of construction, and corrosion. Each section was written by one or more specialists who are well known in their respective fields. Very extensive bibliographies are presented, in which, somewhat unfortunately, the references are listed in order of discussion rather than alphabetically. Author and subject indexes are also provided.

The book is well written and the various fields appear to have been thoroughly covered. The reviews are critical and are not simply a collection of abstracts. Many illustrations of equipment and graphs presenting technical data are included. The book should be particularly useful to one who wants to keep up with progress in the unit operations in a general way or to one who is making a literature survey in a particular field.

Since reviews of unit operations, unit processes, and materials of construction appear regularly in publications written in English, such as " Industrial and Engineering Chemistry," *Fortschritte der Verfahrenstechnik* will probably be of limited interest outside of Germany.

RAYMOND W. SOUTHWORTH

M. S. PETERS : Elementary Chemical Engineering. pp. 322 + ix. McGraw-Hill Book Co. Inc. $6.

THE declared object of this book is to present a unified picture of chemical engineering for persons without experience or training in the subject. This is an ambitious undertaking, and the author has dealt with a wide range of subjects starting with elementary physical chemistry and stoichiometry, following with fluid flow, heat transfer and the unit operations, and concluding with chapters on chemical technology, economics and plant design.

It is difficult to see how so many subjects could receive adequate discussion in a text of 300 pages. In the book under review the theoretical treatment of the unit operations has been condensed by omitting those aspects of the subject which require more than an elementary treatment. The basic equations of heat and mass transfer are presented with little or no discussion of the theoretical principles involved, though their practical application is considered more fully and illustrated with worked examples and problems. In some instances this process of condensation has been carried to a point of absurdity, for example solvent extraction is dealt with in two pages and chemical kinetics receives only half a page. A single chapter of twenty pages is devoted to the description of all types of chemical plant and equipment, ranging from pipe fittings and pumps to evaporators, towers, filters and grinding plant.

The book could be recommended as a useful revision text-book for students receiving a course of tuition and lectures on chemical engineering. However, the uninitiated reader would inevitably gain the impression that chemical engineering comprises a smattering of chemistry, some elementary mathematical exercises and formulae relating to the unit operations, and very little of an engineering nature.

W. S. NORMAN